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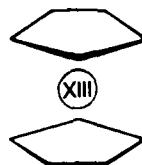
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# XIII International Conference on Organometallic Chemistry

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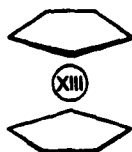


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Torino, September 4-9, 1988

# XIII International Conference on Organometallic Chemistry



Torino, September 4-9, 1988  
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## abstracts

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(FECS event No. 126)

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### XIII INTERNATIONAL CONFERENCE ON ORGANOMETALLIC CHEMISTRY

The Thirteenth 1988 edition of these Conferences is held in Torino, a modern European town of long-standing historical and cultural traditions, in which the brilliant scientist Amedeo Avogadro greatly contributed to establish the foundations of the present-day Chemistry.

Organometallic Chemistry has grown considerably and covers many fields of interest from metal containing supports to biologically relevant molecules. Metal-carbon- and metal-hydrogen bond making and breaking are fundamental steps in many processes of interest to all chemists.

Within the limits imposed by the tight schedule, the Scientific Organizing Committee has tried to aggregate the scientific contributions in meaningful and consistent clusters. The hope is there that the 1988 edition of these Conferences will be a profitable one from a scientific point of view and the wish is extended to all participants for a pleasant and active stay in Torino.

*Fausto Calderazzo*

→ Keywords: Metal Complexes, Ligands, Chemical Bonds, Aromatic Compounds, Porphyrins, Molecular Structure, Photochemical Reactions, Electrochemistry, Surface Chemistry, Crystal Structure, Cyclic Compounds, Synthesis Chemistry, Molecule Molecule Interactions, Ions, Electronic States, Catalysis, Reaction Kinetics, Abstracts.  
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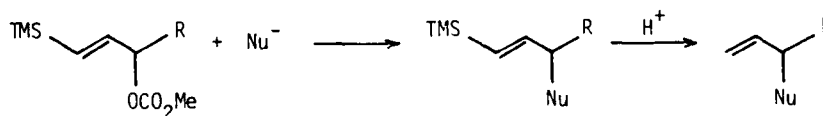
ORAL PRESENTATION



SELECTIVITIES IN ORGANIC REACTIONS  
VIA  $\pi$ -ALLYLPALLADIUM COMPLEXES

Jiro Tsuji, Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

Palladium-catalyzed reactions of various allylic compounds via  $\pi$ -allylpalladium complexes are important synthetic methods. The usefulness of  $\pi$ -allylpalladium chemistry will be expanded if the reactions have high regio- and stereoselectivities. In this lecture, studies on regio- and stereoselectivities in several reactions of allylic carbonates and 2-vinyloxiranes with various nucleophiles are discussed. Particularly it was found that the introduction of trimethylsilyl group to allyl systems showed a profound effect on the regioselectivity of the reaction (ref. 1).



Ref. 1. J. Tsuji, M. Yuhara, M. Minato, H. Yamada, F. Sato, Y. Kobayashi, *Tetrahedron Lett.*, **29**, 343 (1988).

New Reagents for Carbon-hydrogen Activation: Organo-rhodium and -iridium  
Trispyrazolylborates

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T6G 2G2, Canada

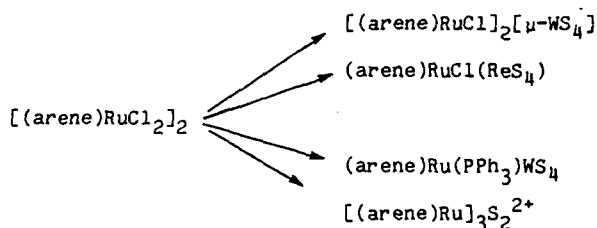
## ARENE RUTHENIUM SULFIDO CLUSTERS

Thomas B. Rauchfuss, Jayantha Amarasekera, Kevin E. Howard, John R.

Lockemeyer, Emmanuel Ramli, Xiaoguang Yang, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801 USA

Although ruthenium carbonyl sulfides are numerous, the corresponding chemistry of arene ruthenium sulfides has not been developed. We have found that compounds of the type  $[(\text{arene})\text{RuCl}_2]_2$  (1) are excellent precursors to this new class of compounds. (Scheme)

Scheme



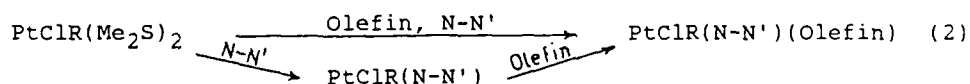
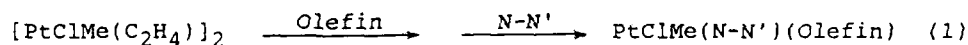
Direct reaction of 1 with salts of  $\text{WS}_4^{2-}$  affords trinuclear compounds of the type  $[(\text{arene})\text{RuCl}]_2(\text{WS}_4)$  which are soluble and thermally stable. Reaction of 1 with  $\text{PPh}_3$  followed by  $\text{WS}_4^{2-}$  gives  $(\text{arene})\text{Ru}(\text{PPh}_3)\text{WS}_4$  which features terminal W=S functionalities. Reaction of 1 with  $\text{ReS}_4^-$  gives purple  $(\text{arene})\text{RuCl}(\text{ReS}_4)$ . Direct reaction of 1 with sulfide gives salts of the closo cluster  $[(\text{arene})\text{-Ru}]_3\text{S}_2^{2+}$ . The structural systematics and reaction chemistry of these compounds will be discussed as well as their potential as precursors to new inorganic polymers.

## FIVE-COORDINATE OLEFIN CARBYL COMPLEXES OF PLATINUM(II)

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Via Mezzocannone 4, 80134 Napoli, Italy

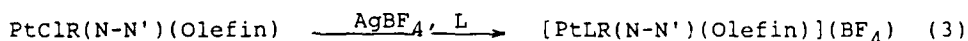
Vincenzo G. Albano, Istituto Chimico G. Ciamician,  
Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

Trigonal bipyramidal complexes of the type  $\text{PtClMe}(\text{N-N}')(\eta^2\text{-C}_2\text{H}_4)$  ( $\text{N-N}' = \alpha, \alpha'$ -bidentate nitrogen ligand) have been recently described. In contrast with the previously known analogs  $\text{PtCl}_2(\text{N-N}')(\text{Olefin})$ , olefin dissociation from the above species was shown to be reversible.<sup>1</sup> With the help of this remarkable property, we have prepared a wide series of related complexes and investigated the influence of the coordination environment on their stability. The syntheses are outlined in eq. 1-3.



(L = neutral ligand)

(R = Alkyl or Aryl ligand)



The equilibria  $\text{PtXR}(\text{N-N}')(\text{Olefin}) \xrightleftharpoons{K} \text{PtXR}(\text{N-N}') + \text{Olefin}$  have been investigated through qualitative and quantitative observations (e.g. determination of K by  $^1\text{H}$  NMR analysis of equilibrium mixtures). The main ligand effects may imply a variation of K of several orders of magnitude and are the following:

a) A dominating factor is the steric hindrance present on both sides of the  $\text{N-N}'$  ligand. If properly oriented in the coordination plane, this tends to stabilize the bipyramidal complexes through a corresponding destabilization of the square-planar species.

b) Electron-releasing substituents on the olefinic double bond destabilize the complexes while electron-withdrawing groups stabilize them. Since literature data suggest the opposite trend for square planar species,<sup>2</sup> this gives a direct evidence of the increased relative importance of  $\pi$ -back-donation in five-coordinate complexes.

Work supported by MPI

1) Albano, V.G.; Braga, D.; De Felice, V.; Panunzi, A.; Vitagliano, A. Organometallics **1987**, 6, 517.

2) Kurosawa, H.; Asada, N. J. Organomet. Chem. **1981**, 217, 259.

## CONJUGATE ADDITION OF ORGANOCOPPER COMPOUNDS AND IODOTRIMETHYLSILANE TO ENONES AND ENOATES

Mikael Bergdahl, Eva-Lotte Lindstedt, Martin Nilsson and Thomas Olsson

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The presentation concentrates on the conjugate addition of organocopper compounds solubilised with tributylphosphine in the presence of iodotrimethylsilane, a reaction which gives high yields under mild conditions, the silyl enol ethers being the primary products.



The work is an extension of our recent findings that lithium iodide is important for the conjugate addition of organocopper compounds in the presence of chlorotrimethylsilane [1]. This led us to use organocopper-iodotrimethylsilane combinations in ether, THF and even dichloromethane to give good yields of the conjugate adducts, primarily as silyl enol ethers [2]. The latter reactions led to homogeneous solutions in the presence of dimethyl sulphide, since the copper iodide formed immediately dissolved.

We now show that presence of tributylphosphine provides homogeneous reactions and even higher yields. The phosphine stabilises and solubilises the copper compound and also seems to favour the addition. The *E/Z*-selectivity in the reactions are affected by the presence of lithium iodide. NMR spectra of reagents, reaction mixtures and products indicate interactions for example between halosilane and organocopper reagents. The mechanism can be discussed in terms of activation of the organocopper compound by iodotrimethylsilane, 3,4-addition to the enone (or enoate) and elimination of copper iodide with formation of the (*E*) silyl enol ethers (in the absence of lithium iodide).

The results provide further improvements of recent methods for activation of lithium organocuprates and of organocopper compounds with chlorotrimethylsilane and complexing agents like HMPA and DMAP [3-5]. The reaction also bridges the gap between the classical conjugate additions and the cross-coupling of organocopper reagents with organic halides in the presence of soft phosphines [6]. In the present reactions the organic group from the soft copper connects to the beta carbon of the enone, the hard silicon connects to the oxygen and copper iodide is formed.

[1] Lindstedt, E.-L., Nilsson, M. and Olsson, T., *J. Organometal. Chem.* 334 (1987) 255.

[2] Bergdahl, M., Lindstedt, E.-L., Nilsson, M. and Olsson, T., *Tetrahedron* 44 (1988) In press.

[3] Corey, E.J. and Boaz, N.W. *Tetrahedron Lett.* 26 (1985) 6015 and 6019.

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**Studies on the Complexation of Polynuclear Heteroaromatic Nitrogen Ligands to Pentamethylcyclopentadienylrhodium Dication: Nitrogen versus  $\pi$ -Bonding**

Richard H. Fish and Hoon-Sik Kim, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720 USA

Recent studies from our laboratory on the regioselective hydrogenation of polynuclear heteroaromatic nitrogen compounds, with mononuclear rhodium homogeneous catalysts, clearly showed that the nitrogen substrate binds to the rhodium metal center prior to hydrogen transfer to the nitrogen ring. Thus, we speculated that the bonding of the nitrogen heterocyclic ring to the rhodium metal center was an important criterion for selective hydrogenation.

Therefore, we wanted to determine the exact nature of nitrogen substrate bonding to the rhodium metal center, i. e., nitrogen (N) versus  $\pi$ -bonding and initiated studies on the reactions of several representative polynuclear heteroaromatic nitrogen ligands with pentamethylcyclopentadienylrhodium dication [ $\text{Cp}^*\text{Rh}^{2+}$ ]. Accordingly, the nitrogen ligands, quinoline, **1**; isoquinoline, **2**; 1,2,3,4-tetrahydroquinoline, **3**; 2-methylquinoline, **4**; N-methylindole, **5**; and N-methylpyrrole, **6**; were reacted with  $\text{Cp}^*\text{Rh}^{2+}$  to provide N-bonding for **1** and **2**, while **3-6** preferred  $\pi$ -bonding.

The relative order of N ligand reactivity, in competitive experiments, was  $2 > 3 > 4 \sim 5 > 1$  and shows that steric effects and availability of non-bonding electrons on the N-atom are important parameters that control N- versus  $\pi$ -bonding to  $\text{Cp}^*\text{Rh}^{2+}$ . In addition, the reactions of the  $\text{Cp}^*\text{Rh N}_{1-3}^{2+}$  ( $\text{N}$ = ligands **1-6**) complexes with hydrogen gas and the use of  $\text{Cp}^*\text{Rh}(\text{quinoline})_{1-2}^{2+}$  and its' synthetic precursors,  $\text{Cp}^*\text{Rh}(\text{acetone})_3^{2+}$  and  $\text{Cp}^*\text{Rh}(\text{p-xylene})^{2+}$ , as catalysts for the selective nitrogen ring reduction will also be discussed.<sup>1</sup>

**Reference**

- 1 R. H. Fish and H-S. Kim Organometallics 1988 (Submitted)

\*These studies at LBL were supported by the Director of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U. S. Department of Energy.

# Addition of Ethylene to Dichloro( $\text{Bu}^t_2$ -ethylenediamine)platinum(II).

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The  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_2(\text{N-N})]$  ( $\text{N-N}$  = bidentate N-donor ligand) represent a well established class of 5-coordinate platinum compounds known since 1973.<sup>1</sup> They are prepared by reacting the chelating ligand with a 4-coordinate platinum(II) species already containing the ethylene ligand; moreover, they can undergo irreversible dissociation of the olefin and formation of  $[\text{PtCl}_2(\text{N-N})]$  species.<sup>2</sup> More recently, it has been reported that substitution of a chloride by a methyl group renders the olefin dissociation reversible, thus providing a new route to this type of complexes.<sup>3</sup> The role of the methyl is not fully understood but it might be related to its strong *trans*-labilizing effect.

The complex  $[\text{PtCl}_2(\text{Bu}^t_2\text{en})]$  is anomalous in the series of dichloroplatinum(II) complexes with substituted ethylenediamines. For instance, in DMSO, it adds one molecule of solvent without dissociating a chloride ion.

The *cis* isomer of  $[\text{PtCl}_2(\text{Bu}^t_2\text{en})]$ , **1**, (*cis* is referred to the conformation of the bidentate ligand), reacts in chloroform (containing ca. 1% of ethanol) with ethylene under pressure (7 atm) forming the corresponding five-coordinate species  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_2(\text{Bu}^t_2\text{en})]$ , **2**, under our experimental conditions the reaction leads to a 1:2 ratio of ca. 6:4. The solution is capable to catalyze ethylene polymerization with formation of paraffins having an average molecular weight of 300.

Other strictly related complexes such as  $[\text{PtCl}_2(\text{Pr}^i_2\text{en})]$  and  $[\text{PtCl}_2[(\text{MePhHC})_2\text{en}]]$  under the same experimental conditions do not give formation of detectable amount of the five-coordinate species.

Different aspects of the olefin addition and polymerization will be discussed.

Work supported by the Consiglio Nazionale delle Ricerche, Roma.

<sup>1</sup>L. Cattalini, F. Gasparrini, L. Maresca, and G. Natile, *J. Chem. Soc. Chem. Commun.*, 369 (1973).

<sup>2</sup>L. Maresca, G. Natile, M. Calligaris, P. Delise, and L. Randaccio, *J. Chem. Soc. Dalton Trans.*, 2386 (1976); A. De Renzi, B. Di Blasio, A. Saporito, M. Scalone, A. Vitagliano, *Inorg. Chem.*, **19**, 960 (1980). H. van der Poel, G. van Koten, M. Kokkes, C. H. Stam, *Inorg. Chem.*, **20**, 2941 (1981).

<sup>3</sup>V. G. Albano, O. Braga, V. De Felice, A. Panunzi, and A. Vitagliano, *Organometallics*, **6**, 517 (1987). A. De Renzi, G. Morelli, A. Panunzi, and A. Vitagliano, *Gazz.Chim.Ital.*, **107**, 549 (1987).

# ALKOXIDE COMPLEXES OF GROUP 6 METALS AND THEIR FORMATION FROM THE CORRESPONDING HYDRIDES.

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The loss of an aldehyde RCHO from an alkoxide RCH<sub>2</sub>OM is not always thermodynamically downhill; the  $\text{RCH}_2\text{OM} \rightleftharpoons \text{RCHO} + \text{H-M}$  equilibrium may lie to the left, even with ordinary aldehydes. However, a RCHO/H-M mixture may be kinetically stable, with acid catalysis required in order for the thermodynamically favored RCH<sub>2</sub>OM to be formed. CpMo(CO)<sub>3</sub>H does not react with aldehydes in the absence of acid, but in the presence of CF<sub>3</sub>CO<sub>2</sub>H it reacts with CH<sub>3</sub>CHO and ArCHO (Ar = Ph, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>). With CH<sub>3</sub>CHO, CpMo(CO)<sub>3</sub>Et can be seen by NMR; the alkoxides formed from the other aldehydes are converted to the corresponding alcohol or ether by the acid present.

Alkoxide complexes of this type can be isolated after careful deprotonation of the corresponding alcohol complex. For example, [CpW(CO)<sub>3</sub>(EtOH)]BF<sub>4</sub> can be made from solid CpW(CO)<sub>3</sub>BF<sub>4</sub><sup>1</sup> and ethanol vapor; when a toluene solution of [CpW(CO)<sub>3</sub>(EtOH)]BF<sub>4</sub> is treated with proton sponge at room temperature, [CpW(CO)<sub>2</sub>(μ-OEt)]<sub>2</sub> is formed.

<sup>1</sup>Beck, W.; Schlöter, K. Z. *Naturforsch.* 1978, 33b, 1214.

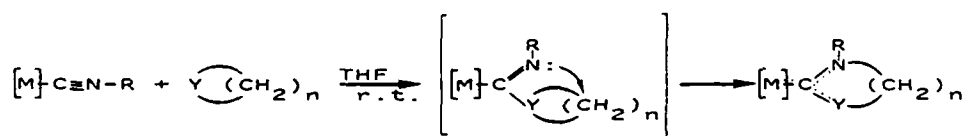


SYNTHESIS OF 5- and 6- MEMBERED CYCLIC CARBENE COMPLEXES DERIVED FROM ISOCYANIDE  
LIGANDS IN COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

Roberta Bertani, Mirto Mozzon, and Rino A. Michelin

Centro di Chimica Metallorganica C.N.R. and Istituto di Chimica Industriale,  
Facolta' di Ingegneria, Universita' di Padova, 35100 Padova, Italy

Recently we reported<sup>1</sup> that metal-stabilized 5-membered cyclic aminoxy- and diaminocarbene complexes can be prepared by reaction of 2-bromoethanol and 2-bromoethylamine hydrobromide in the presence of *n*-BuLi with isocyanide ligands in complexes of Pd(II) and Pt(II). By taking advantage of the tendency of highly strained 3-membered heterocycles  $\overline{YCH_2CH_2}$ , where Y=NH (aziridine), S (thiirane), O (oxirane) and 4-membered heterocycle  $\overline{HNCH_2CH_2CH_2}$  (azetidine), to undergo ring opening reactions, we have studied the following reactions of electrophilic isocyanide ligands in certain complexes of Pd(II) and Pt(II) :



$[M]$  = Pd(II), Pt(II); R = alkyl, aryl; n=2, Y=NH, S, O ; n=3, Y=NH

In contrast to similar reactions of CO and CS ligands which require the presence of a halide salt as catalyst<sup>2</sup>, the reactions of RNC ligands proceed spontaneously at room temperature to give 5- and 6-membered cyclic carbenes. The proposed reaction mechanisms as well as the spectroscopic data of the cyclic carbene products are discussed.

References

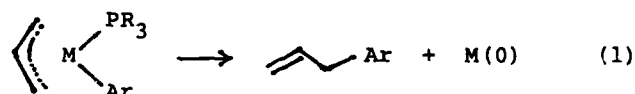
- 1 Michelin, R.A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R.J. *Inorg.Chem.* 1988, 27, 85. *Idem*, *Ibidem*, 1988, 27, 93
- 2 (a) Singh, M.M.; Angelici, R.J. *Angew.Chem.Int.Ed.Engl.* 1983, 22, 163.  
(b) Singh, M.M.; Angelici, R.J. *Inorg.Chem.* 1984, 23, 2691. (c) *Idem*, *Ibidem*, 1984, 23, 2699. (d) Singh, M.M.; Angelici, R.J. *Inorg.Chim. Acta* 1985, 100, 57.

NEW ASPECTS IN REDUCTIVE ELIMINATION OF  
 $\pi$ -ALLYL COMPLEXES OF GROUP 10 METALS

Hideo Kurosawa, Yoshikane Kawasaki, Shinji Murai

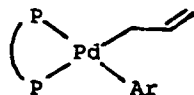
Department of Applied Chemistry, Osaka University, Suita,  
 Osaka 565, Japan

Herein reported are new reactivity trends in reductive elimination of  $\pi$ -allylmetal complexes **1** which are relevant to the full understanding and rational design of metal catalyzed allylic alkylation and olefin oligomerization reactions. The reactivity



**1** (M= Ni, Pd, Pt)

in eq. 1 follows the order, M= Ni > Pd >> Pt. Adding excess monophosphine ligand to the nickel and palladium complexes resulted in no significant acceleration nor retardation of the rate. On the other hand, addition of a chelating diphosphine caused retardation of eq. 1 in the case of the palladium complex, but ca.  $10^8$  times acceleration in the case of the nickel analog. These contrasting behaviors are unambiguously attributed to the formation of the less reactive  $\sigma$ -allylpalladium **2** and the extremely reactive 18-electron  $\pi$ -allylnickel **3**, respectively, each of **2** and **3** having been fully characterized separately.



**2**



**3**

## THE PREPARATION OF NICKEL TRIAD METAL YLIDE COMPLEXES

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Sulfur ylide complexes were obtained in high yields by the reaction of trimethylsulfoxonium iodide with  $M(PR_3)_2Cl_2$  ( $M = Pt, Pd, R = Me \text{ or } Ph$ ) under basic condition by the phase transfer catalysis (PTC) technique. Detailed reaction conditions were examined. The optimal range of base was found between 2.5N and 1N. Increasing the amount of phase transfer catalyst enhanced the rate of complex formation. Without a phase transfer catalyst, sulfur ylide complexes were obtained in low yield. The proposed role of the phase transfer catalyst is to carry the  $OH^-$  into the organic layer and to prevent the ylide abstracting a proton from water contained in the organic phase. The preparation of other metal ylide complexes, including mixed ylide metal complexes will be described.

**BINUCLEAR COPPER(I) COMPLEXES CONTAINING ONE, TWO OR THREE  
2-(DIPHENYLPHOSPHINE)PYRIDINE ( $\text{Ph}_2\text{Ppy}$ ) BRIDGING LIGANDS. SYNTHESIS  
OF NEW PHOSPHORUS YLIDE COMPLEXES OF COPPER(I)**

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Maurizio Lanfranchi and Antonio Tiripicchio, Istituto di Chimica  
Generale ed Inorganica, Università di Parma, Centro di Studio per  
la Strutturistica Diffraattometrica del CNR, Viale delle Scienze,  
43100 Parma, Italy.

Treatment of  $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$  complex with 2-(diphenylphosphi-  
ne)pyridine ( $\text{Ph}_2\text{Ppy}$ ) in dichloromethane at room temperature or  
with an excess of  $\text{Ph}_2\text{Ppy}$  in refluxing acetonitrile affords  $[\text{Cu}_2$   
 $(\mu\text{-Ph}_2\text{Ppy})_2(\text{MeCN})_2][\text{BF}_4]_2$  (I) or  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppy})_3(\text{MeCN})][\text{BF}_4]_2$   
(II), respectively.

The crystal structure of (II) has been determined by a X-ray  
single-crystal diffraction study and provides the first example of  
a new structural type of  $\text{Ph}_2\text{Ppy}$  bridged bimetallic complexes. To  
the best of our knowledge, this is the first example of a copper  
complex containing  $\text{Ph}_2\text{Ppy}$  ligands and the first example of a  
binuclear complex with three  $\text{Ph}_2\text{Ppy}$  ligands.

$^1\text{H}$  and  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. studies at room temperature show that MeCN  
and  $\text{Ph}_2\text{Ppy}$  dissociation followed by rapid ligand exchange  
processes take place in solution.

The lability of the MeCN ligand in complex (II) as well as the  
presence of one co-ordinatively unsaturated copper atom allows the  
synthesis of the substituted complexes  $[\text{Cu}_2(\mu\text{-Ph}_2\text{Ppy})_3\text{L}_x][\text{BF}_4]_2$  ( $x$   
= 1, L = 2-methylpyridine;  $x$  = 2, L =  $\text{P}(\text{OMe})_3$ ,  $\text{PMe}_3$  and  
4-methylpyridine). No reaction is observed with carbon monoxide  
and 1-phenyl-1-propyne.

Complexes (I) and (II) react with anionic bidentate phosphorus  
ylide ligands,  $[(\text{CH}_2)_2\text{PR}_2]^-$  ( $\text{R} = \text{Ph}, \text{Me}$ ), to give new copper(I)  
ylide complexes.

MULTINUCLEAR MAGNETIC RESONANCE STUDIES OF PHOSPHINE AND  
ISONITRILE SUBSTITUTED DERIVATIVES OF  $\text{Co}_4(\text{CO})_{12}$

S.A. Kernaghan, B.T. Heaton and J.A. Iggo, Department of Chemistry,  
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Multinuclear ( $^{59}\text{Co}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ ) n.m.r. studies have been performed on  $\text{Co}_4(\text{CO})_9(\text{tripod})$  [ $\text{tripod} = \text{HC}(\text{PPh}_2)_3$ ] and  $\text{Co}_4(\text{CO})_9(\text{triphos})$  [ $\text{triphos} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ] and  $\text{Co}_4(\text{CO})_{12-n}\text{L}_n^{\frac{1}{2}}$  [ $\text{L} = \text{MeNC}$  or  $\text{Bu}^t\text{NC}$ ;  $n = 1, 2, 3$ ].

The solution structure of  $\text{Co}_4(\text{CO})_9(\text{triphos})$  has been determined by  $^{13}\text{C}$  and  $^{31}\text{P}$  n.m.r. and is analogous to that previously found for  $\text{Co}_4(\text{CO})_9(\text{tripod})$ .<sup>2</sup>  $^{13}\text{C}$  n.m.r. saturation transfer experiments<sup>3</sup> have been used to follow the processes by which CO scrambling occurs in these clusters.

$^{13}\text{C}$  n.m.r. studies of  $\text{Co}_4(\text{CO})_{12-n}\text{L}_n^{\frac{1}{2}}$  have been used to establish the site of CO substitution.

The effect on the value of  $\delta(^{59}\text{Co})$  and  $w_{1/2}$  of the  $^{59}\text{Co}$  resonance resulting from ligand substitution of clusters is found to depend on the nature of the ligand. For triphosphine ligands there is only a small shift of  $\delta(^{59}\text{Co})$  for the basal and apical resonances, but there is a noticeable narrowing of the basal  $^{59}\text{Co}$  resonance. Substitution of CO by isonitrile ligands does not significantly affect  $w_{1/2}$  of the basal and apical  $^{59}\text{Co}$  resonances but there is a large shift of  $\delta(^{59}\text{Co})$  for the apical  $^{59}\text{Co}$  resonance and little effect on the basal  $^{59}\text{Co}$  chemical shift.

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REACTIVITY OF  $[\text{Ir}_6(\text{CO})_{15}]^{2-}$  WITH COMPLEXES OF  
THE METALS OF THE IB AND IIB GROUPS.

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The reactions of the dianion  $[\text{Ir}_6(\text{CO})_{15}]^{2-}$  with complexes of the metals of the IB and IIB groups have been investigated. The cluster anion reacts at room temperature with  $\text{HgCl}_2$  to give  $[\text{Ir}_6(\text{CO})_{15}\text{HgCl}]^-$  (I) in quantitative yields. Its structure consists of an octahedron of iridium atoms capped by a  $\text{HgCl}$  moiety and bearing twelve terminal and three face bridging carbonyls. This arrangement is closely related to that found in the red isomer of  $[\text{Ir}_6(\text{CO})_{16}]$  [1]. The same reaction performed with  $\text{EtHgCl}$  affords, in a first step, anion (I), and on standing, evolves giving  $[\text{Ir}_6(\text{CO})_{14}(\text{HgCl})_2]^{2-}$  which contains two face bridging  $\text{HgCl}$  groups.  $[\text{Ir}_6(\text{CO})_{15}]^{2-}$  reacts very slowly with  $\text{Au}(\text{PPh}_3)\text{Cl}$  or  $\text{Cu}(\text{PPh}_3)\text{Cl}$ , and after 48 h only a 30% conversion could be observed even in the presence of a large excess of complex. On the other hand, the cation  $[\text{Au}(\text{PPh}_3)_3]^+$  reacts immediately and quantitatively to give  $[\text{Ir}_6(\text{CO})_{15}\text{Au}(\text{PPh}_3)]^-$ .

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**Intramolecular Dynamics Of Cluster Compounds Derived from  
Ir<sub>4</sub>(CO)<sub>12</sub> and Ir<sub>2</sub>Rh<sub>2</sub>(CO)<sub>12</sub>.**

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The following series of cluster compounds were examined by 2D and variable temperature <sup>13</sup>C-NMR and <sup>31</sup>P-NMR : [Ir<sub>4</sub>(CO)<sub>11</sub>Br]<sup>-</sup>, I; Ir<sub>4</sub>(CO)<sub>11</sub>(μ<sub>2</sub>-SO<sub>2</sub>), II; Ir<sub>4</sub>(CO)<sub>10</sub>(PMePh<sub>2</sub>)<sub>2</sub>, III; Ir<sub>4</sub>(CO)<sub>10</sub>(μ<sub>2</sub>-dppm), IV; Ir<sub>2</sub>Rh<sub>2</sub>(CO)<sub>10</sub>(μ<sub>2</sub>-dppm), V; Ir<sub>4</sub>(CO)<sub>10</sub>(μ<sub>2</sub>-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>), VI; Ir<sub>4</sub>(CO)<sub>10</sub>(μ<sub>2</sub>-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>5</sub>PPh<sub>2</sub>), VII; Ir<sub>4</sub>(CO)<sub>10</sub>(diars), VIII; Ir<sub>4</sub>(CO)<sub>10</sub>(1,5-cyclooctadiene), IX; Ir<sub>4</sub>(CO)<sub>9</sub>(diars)(PPh<sub>3</sub>), X; Ir<sub>4</sub>(CO)<sub>9</sub>(L<sub>3</sub>), XI and XII; Ir<sub>2</sub>Rh<sub>2</sub>(CO)<sub>9</sub>(L<sub>3</sub>), XIII, XIV (L<sub>3</sub> = (Ph<sub>2</sub>P)<sub>3</sub>CH, S<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>), and Ir<sub>4</sub>(CO)<sub>8</sub>(μ<sub>2</sub>-dppm)<sub>2</sub>, XV.

The observed fluxional processes are all due to CO site exchange and fall into 4 categories :

1. The "merry-go-round" of basal CO's. This process is of lowest activation energy for the Ir<sub>4</sub> clusters (I, IV, VI, XI, XII), but not for the Ir<sub>2</sub>Rh<sub>2</sub> clusters (V, XIII, XIV). The unbridged "intermediate" of this process was in fact observed as a stable isomer for XII.
2. A switch of basal face by edge-bridging of 3 CO's to an alternative face of the tetrahedral metal core. This process occurs in all monosubstituted complexes. In the disubstituted complexes, it may occur when the non-CO ligands occupy two stereochemically different positions. The site exchange proceeds via an unbridged intermediate (IX, first process of XV) or is concerted (I, II, VIII, X).
3. A rotation of apical CO's : this process is of highest activation energy for the Ir<sub>4</sub> clusters (II, XI, XII), but of lowest energy for the Ir<sub>2</sub>Rh<sub>2</sub> clusters (IV, XIII, XIV).
4. Edge-bridging of 3 radial CO's on the basal face . This unprecedented process is the simplest explanation of the P site exchange in VII : the axial and radial P atoms exchange without any switch of basal face (the apical CO's remain apical, the bridged ones remain bridged).

SYSTEMATIC SYNTHESIS OF  $[\text{M}(\text{Ir}_4(\text{CO})_9\text{L}(\eta^5\text{-C}_5\text{Me}_5)(\mu_4\text{-PPh}))]$  ( $\text{M}=\text{Rh}$ ,  $\text{Ir}$  AND  $\text{L}=\text{CO}$ ,  $\text{PPh}_3$ ,  $\text{PPh}_2\text{Me}$  AND  $\text{PPhMe}_2$ );  $^{13}\text{C}$  nmr ( $\text{L}=\text{CO}$ ) AND X-RAY ANALYSIS OF  $[\text{Ir}_5(\text{CO})_{10}(\eta^5\text{-C}_5\text{Me}_5)(\mu_4\text{-PPh})]$

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The deprotonation reactions of  $[\text{Ir}_4(\text{CO})_{11}(\text{PPhH}_2)]$  and  $[\text{Ir}_4(\text{CO})_{10}\text{L}(\text{PPhH}_2)]$  in the presence of  $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)(\text{MeCN})_3][\text{SbF}_6]_2$ , give high yields of  $[\text{M}(\text{Ir}_4(\text{CO})_{10}(\eta^5\text{-C}_5\text{Me}_5)(\mu_4\text{-PPh}))]$ , ( $\text{M}=\text{Rh}$ (1a),  $\text{Ir}$ (1b)), and  $[\text{M}(\text{Ir}_4(\text{CO})_9\text{L}(\eta^5\text{-C}_5\text{Me}_5)(\mu_4\text{-PPh}))]$  ( $\text{M}=\text{Rh}$ (2a),  $\text{Ir}$ (2b);  $\text{L}=\text{PPh}_3$ ,  $\text{PPh}_2\text{Me}$  and  $\text{PPhMe}_2$ ) respectively. Direct CO substitution on (1a) and (1b), either by oxidation of CO with  $\text{Me}_3\text{NO}$  in the presence of L, or by reaction with  $[\text{Bu}_4\text{N}][\text{Br}]$  followed by  $\text{Br}^-$  abstraction with  $\text{Ag}^+$  in the presence of L, also yields (2a) and (2b) respectively. The role of the PPh ligand in the condensation and CO substitution reactions will be discussed.

X-ray analysis of (1b) reveals a square-based pyramidal arrangement of Ir atoms, with the  $\mu_4\text{-PPh}$  ligand capping the square face. The slow exchange limiting  $^{13}\text{C}$  nmr spectra of (1a) and (2b) are consistent with the solid state structure; a structure is proposed for (2a) and (2b) and possible mechanisms for the CO fluxionality in all these species will be proposed.



## On the Relative Strengths of Metal-Alkyl and Metal-Hydrogen Bonds .A Theoretical Study Based on Density Functional Theory.

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M-R bond formation ( $R=H, \text{alkyl}$ ) and M-R cleavage pervades most of the elementary reaction steps in organometallic chemistry, and the difference in M-H and M-alkyl bond strengths has important implications for the relative ease with which ligands insert into the two types of bonds as well as the facility with which  $H_2$  can add oxidatively to a metal center in comparison with H-alkyl and alkyl-alkyl bonds.

We present here calculations on M-H and M- $CH_3$  bond energies in a number of representative  $RML_n$  complexes, encompassing early  $[Cp_2MR]$  ( $M=Sc, La, Y$ ) as well as middle  $[Cp_2VR, Mn(CO)_5R, \text{ and } CpCr(CO)_3R]$  to late  $[CpNi(CO)R]$  transition metal and f-block elements  $[Cp_2MCIR]$  ( $M=Th, U$ ).

The main objective in this study has been to augment the scanty (and inaccurate) experimental data with near quantitative theoretical estimates of M-R bond energies for the whole spectrum of transition metals and f-block elements. We shall further explain why M-H and M- $CH_3$  bonds are quite similar in strengths for f-block elements and early transition metals, whereas M-H bonds are much stronger (by  $50 \text{ kJ mol}^{-1}$ ) than M- $CH_3$  bonds for middle to late transition metals. Trends in the M-R bond strengths within a triad of transition metals will also be discussed.

LIGAND DEPENDENT NATURE OF THREE POSSIBLE  
SHAPES FOR A  $d^6$  PENTACOORDINATED COMPLEX

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The distortion of model  $XMH_4 d^6$  complexes (X-equatorial ligand) away from their unstable trigonal bipyramidal (TBP) structure is studied by means of Extended Hückel calculations. The distortion is represented by the angle  $\alpha$  between the two equatorial M-H bonds ( $\alpha = 120^\circ$  in the TBP geometry). Departure from  $\alpha = 120^\circ$  leads to two minima, one for  $\alpha = 180^\circ$  (square pyramid geometry) and one for  $\alpha = 70^\circ$ , the origin of both being traced to a first order Jahn-Teller effect and not to a favourable ligand-ligand interaction ( $\alpha = 70^\circ$ ). The relative energies of these two minima are strongly dependent on the nature of the equatorial ligand X opposite to the  $\alpha$  angle. In particular it is shown that a  $\pi$  donor X ligand favours  $\alpha = 70^\circ$  while a  $\pi$  acceptor favours  $\alpha = 180^\circ$ . Finally a third minima is found for  $\alpha = 30^\circ$ . In this case, there is a strong interaction between the equatorial hydrides and this structure is better viewed as a  $d^8$  square planar complex with a molecular  $H_2$  ligand side-bonded to the metal.

A NEW APPROACH TO MEASURING ABSOLUTE METAL-LIGAND BOND DISRUPTION ENTHALPIES  
IN ORGANOMETALLIC COMPOUNDS. THE  $\{(\text{CH}_3)_3\text{SiC}_5\text{H}_4\}_3\text{U}$ - SYSTEM

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Absolute uranium-ligand bond disruption enthalpies in the series  $\text{Cp}_3\text{UR}$  ( $\text{Cp} = \eta^5\text{-Me}_3\text{SiC}_5\text{H}_4$ ) have been measured by halogenolytic isoperibol titration calorimetry of  $\text{Cp}_3\text{U/Cp}_3\text{UI/Cp}_3\text{UR}$  ensembles. Derived  $D(\text{Cp}_3\text{U-R})$  values in toluene solution are (kcal/mol, R): 62.4(0.4) (I); 28.9(1.7) (n-Bu); 25.6(3.1) (Bz); 39.3(2.3) ( $\text{CH}_2\text{SiMe}_3$ ); 44.8(1.1) (Me); 48.5(2.2) (vinyl); 87.2 (C=CPh).  $D(\text{Cp}_3\text{U-L})$  values (kcal/mol, 95% confidence limits) in toluene solution were also determined for L = CO (10.3(0.2)) and THF (9.8(0.2)). The magnitudes of the  $D(\text{U-R})$  values appear to reflect a combination of steric and electronic factors, and strongly suggest that  $D(\text{U-I})$  is less sensitive to ancillary ligation (more transferable) than  $D(\text{U-alkoxide})$ . The complex  $\text{Cp}_3\text{U}(\text{vinyl})$  crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in a unit cell of dimensions  $a = 11.298(1)$ ,  $b = 13.997(2)$ ,  $c = 9.460(2)$  Å, and  $\alpha = 97.00(1)^\circ$ ,  $\beta = 105.98(1)^\circ$ , and  $\gamma = 86.94(1)^\circ$ . Least-squares refinement led to a value for the conventional R index (on F) of 0.0196 for 4373 reflections having  $2\theta_{\text{MoK}\alpha} < 50^\circ$  and  $I > 3\sigma(I)$ . The molecule possesses a conventional pseudotetrahedral  $\text{Cp}_3\text{MX}$  geometry with  $\text{U-C}(\text{ring}) = 2.759(4)$  Å (average),  $\text{U-C}(\alpha, \text{vinyl}) = 2.436(4)$  Å,  $\angle \text{U-C}(\alpha, \text{vinyl})\text{-C}(\beta, \text{vinyl}) = 137.7(3)^\circ$ ,  $\angle \text{Cg-U-Cg} = 116.4^\circ$ ,  $117.2^\circ$ ,  $120.0^\circ$ , and  $\angle \text{Cg-U-C}(\alpha, \text{vinyl}) = 95.1^\circ$ ,  $100.0^\circ$ ,  $100.1^\circ$ . All hydrogen atoms were located, and  $\text{U-H}(\text{C}\alpha, \text{vinyl}) = 2.93(4)$  Å. The metrical parameters evidence severe nonbonded repulsions between the vinyl ligand and the Cp ligands, as well as between different Cp ligands. The quantity  $D(\text{M-I})\text{-}D(\text{M-CH}_3)$  is proposed as a new gauge of metal-ligand bonding.

HOMOLEPTIC ALKYL AND ALKOXID OF THE TRANSITION ELEMENTS-  
MOLECULAR STRUCTURE AND BONDING

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The molecular structure of monomeric  $\text{Cr}(\text{CH}_2\text{CMe}_3)_4$ ,  $\text{Cr}(\text{OBu}^t)_4$ , and  $\text{W}(\text{OMe})_6$  ( $\text{Me}=\text{CH}_3$ ) has been determined by gas electron diffraction.

The best model for  $\text{W}(\text{OMe})_6$  has a  $\text{WO}_6$  symmetry of  $\text{O}_h$ , the relative orientation of the ligands is difficult to determine. The W-O bond distance is 190.7(1)pm, the W-O-C angle is 132.4(6) $^\circ$ .

The best model has  $\text{S}_4$  symmetry for both chromium compounds, any distortion from  $\text{T}_d$  symmetry of the  $\text{CrO}_4$  and  $\text{CrC}_4$  in a  $\text{D}_{2d}$  manner cannot be seen from the data. The Cr-C distance is 203.8(6)pm, with a Cr-C-C angle of 128.0(8) $^\circ$ . The Cr-O distance is 176(2)pm, with a Cr-O-C angle of 140(1) $^\circ$ .

Ab-Initio HF-SCF and CASSCF calculations are carried out to study the nature of the transition metal-ligand bond.

We also hope to present recent results concerning the molecular structure of  $\text{Zr}(\text{CH}_2\text{CMe}_3)_4$ ,  $\text{Ti}(\text{NMe}_2)_4$ ,  $\text{TiMeCl}_3$  and  $\text{V}(\text{OBu}^t)_4$ .

# Geometry Deformations in A-PZ<sub>3</sub> Compounds: A Structural Test of Theories of Bonding in Phosphine Complexes.

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The widespread application of phosphines and their derivatives in industrial and academic organometallic chemistry makes an understanding of how they bind to metals, and other substrates, of great importance. This paper reports ways of using crystallographic data to assess current theories of bonding in phosphine complexes.

The large number of compounds in which triphenylphosphine (PPh<sub>3</sub>) is present as a clearly defined fragment make it a suitable test case for the assessment of bonding theory of phosphines in general. We have used the Cambridge Structural Database as a source of information on how the PPh<sub>3</sub> fragment is distorted by complexation to an atom A, where A may be a *d*- or *p*-block metal or other *p*-block element such as C, N or O. Our strategy has been to examine the variation in the structure of the PPh<sub>3</sub> fragment in A-PPh<sub>3</sub> species as revealed by the A-P and P-C bond lengths, and the C-P-C and A-P-C angles.

While a number of statistical approaches are possible, we have concentrated on two.

- i) The mean P-C length ( $\langle r \rangle$ ) was plotted against mean C-P-C ( $\langle \alpha \rangle$ ) for each element A. This shows strong correlation between  $\langle r \rangle$  and  $\langle \alpha \rangle$  (correlation coefficient ca. -0.95), and a marked dependency of  $\langle r \rangle$  and  $\langle \alpha \rangle$  on A. Small and electronegative A (e.g. O, N, H) leads to  $\langle r \rangle$  being short (and  $\langle \alpha \rangle$  large). Conversely large, electropositive A (e.g. Cr, Re, Ru) are associated with long  $\langle r \rangle$  (and small  $\langle \alpha \rangle$ ).
- ii) Correlations, between the A-P and P-C bond lengths (*d* and *r* respectively) and between *d* and C-P-C angle ( $\alpha$ ) were analysed. These showed a range of behaviour, notably for the *d*-block metals. For elements in the centre and left of the transition series  $\alpha$  and *d* are positively correlated, while at the right  $\alpha$  and *d* are negatively correlated.

In a separate study we have examined the effect of oxidation of the transition metal in M-PZ<sub>3</sub> complexes on *d*, *r* and  $\alpha$ . This shows the importance of M-P  $\pi$ -bonding on both M-P and PZ<sub>3</sub> geometries.

These observations are compared with predictions based on electronic and "steric" theories of molecular structure as applicable to tertiary phosphine complexes.

## ORIENTATION EFFECTS ON ALKALI METAL REACTIONS WITH ALKYL IODIDES

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Iodine is extracted from alkyl iodides by alkali and alkaline earth metals. This preference exhibits a dependence upon the cosine of the "angle of attack,"  $\cos \theta$ , for products which are backscattered in molecular beam experiments. The cutoff angle for this dependence expresses the classical chemical steric effect.

This reaction class is discussed in terms which evolved empirically from a combination of trajectory simulations, crossed molecular beam and laser induced fluorescence experiments. The interpretation suggests that the experimental behavior results from the transfer of an electron from the metal to the alkyl iodide at large distances, followed by a repulsive release of exothermicity. This mechanism is consistent with the observed small energies of activation, large reaction probabilities, and a correlation of product excitation with the mass of the alkyl group. The reaction is predicted to become orientation independent at large impact parameters. However, experimental verification of this prediction is incomplete.

Quality ab initio information on this system is not available, however, it has been the subject of a semi-empirical diatomics in molecules (DIM) calculation. Although this system has been simulated several times, only a recent three atom trajectory treatment by Blais and Bernstein exhibits the  $\cos \theta$  sensitivity. A six atom treatment is necessary to examine how explicit inclusion of the hydrogens produces orientation effects; and to properly sample the initial rotational conditions for a symmetric top. Rotation of the target can influence the distribution of orientations which are sampled by the calculation.

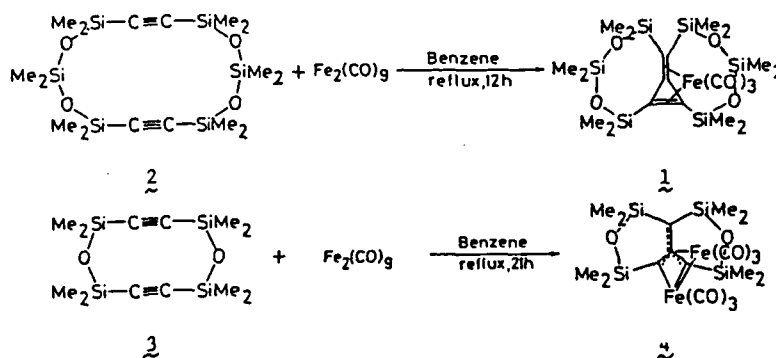
We are representing this system by extending an approach developed by Valencich, Chapman, and Bunker to treat hydrogen atom reactions with methane. This six atom potential extrapolates to the three atom limit described by Blais and Bernstein. The barrier height increases as the approach of the metal deviates from colinearity, the methyl end is unreactive, and the hydrogens are explicitly included. We can also repeat selected trajectories with their three atom Blais and Bernstein approximation. This will help ascertain what aspects of three atom treatments can be extrapolated to larger systems. We will discuss the preliminary dynamics on this surface.

NOVEL IRON CARBONYL COMPLEXES OF METHYLENECYCLOPROPENE AND  
TRIMETHYLENEMETANE. INTERMEDIATES AND MECHANISM

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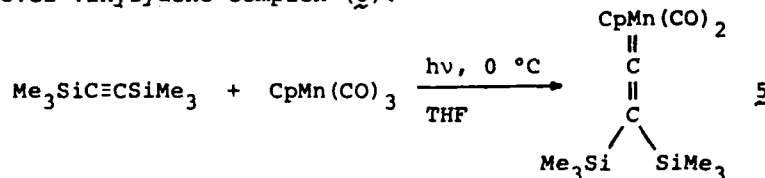
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A novel (methylenecyclopropene)iron tricarbonyl complex (1) was prepared by the reaction of 3,3,5,5,7,7,10,10,12,12,14,14-dodecamethyl-4,6,11,13-tetraoxa-3,5,7,10,12,14-hexasilacyclotetradeca-1,8-diyne (2) with diironnonacarbonyl, as orange crystals, mp 122-123 °C (dec).



On the other hand, the reaction of 3 with Fe<sub>2</sub>(CO)<sub>9</sub> resulted in the formation of a novel trimethylene methane complex (4). Structures of these complexes were determined by X-ray crystallographic analyses together with various spectroscopic properties.

The key step in these reactions is 1,2-silyl migration of complexed bis(silyl)acetylenes. Actually the reaction of bis(trimethylsilyl)acetylene with  $\pi$ -cyclopentadienylmanganese tricarbonyl gave a novel vinylidene complex (5).



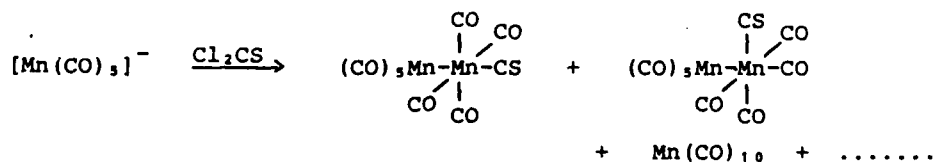
Structures of these interesting new complexes as well as the reaction mechanism will be discussed.

SPECTROSCOPIC EVIDENCE FOR THE FORMATION OF  $\text{Mn}_2(\text{CO})_9\text{CS}$ 

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Although the field of thiocarbonyl complexes has been explored in the last decade, rather few information is available about thio-carbonyl derivatives of simple binary carbonyl compounds of the type  $\text{M}_x(\text{CO})_y$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$  [1];  $\text{M} = \text{Fe}$  [2]).

We have now obtained a  $\text{Mn}_2(\text{CO})_{10}/\text{Mn}_2(\text{CO})_9\text{CS}$  mixture in low yields from the reaction of  $[\text{Mn}(\text{CO})_5]^-$  with thiophosgene in pentane. The thiocarbonyl complex as the minor product (5 to 10%) could not be separated from  $\text{Mn}_2(\text{CO})_{10}$  but was identified by the (CS) frequencies in the IR spectrum at 1300 and 1280  $\text{cm}^{-1}$  and by mass spectroscopic measurements. The results were indicative for the presence of two isomers possessing the CS ligand either in trans position to CO or to the  $\text{Mn}(\text{CO})_5$  group.



Reaction of the mixture with  $\text{Br}_2$  gave mainly  $\text{Mn}(\text{CO})_5\text{Br}$  along with small amounts of  $\text{Mn}(\text{CO})_4(\text{CS})\text{Br}$  which was identified by IR and mass spectroscopy. A product containing CS could also be identified from the reaction of the mixture with  $\text{PPh}_3/\text{ONMe}_3$ .

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## SULFUR MONOXIDE AS A LIGAND IN TRANSITION METAL COMPLEXES

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Mononuclear sulfur monoxide complexes of iron, rhodium, and iridium are readily obtained by transition metal-induced cleavage of ethylene episulfoxide (1). The close similarity between these compounds and analogous complexes of sulfur dioxide can be explained on the basis of a simple MO picture. Reactions investigated so far include coordinative and oxidative addition as well as nucleophilic and electrophilic attack at sulfur. Treatment of the square-planar complexes  $MCl(PR_3)_2(SO)$  ( $M = Rh, Ir$ ) with CO leads to the liberation of SO which can be trapped by addition to orthoquinones at low temperature. A method will also be described for the catalytic cleavage of episulfoxides which allows the use of the highly unstable and reactive sulfur monoxide as a synthetic reagent.

(1) W. A. Schenk, *Angew. Chem.* 99 (1987) 101; *Angew. Chem. Int. Ed. Engl.* 26 (1987) 98.

## SULFUR MONOXIDE, A NEW AND VERSATILE LIGAND IN ORGANOMETALLIC CHEMISTRY

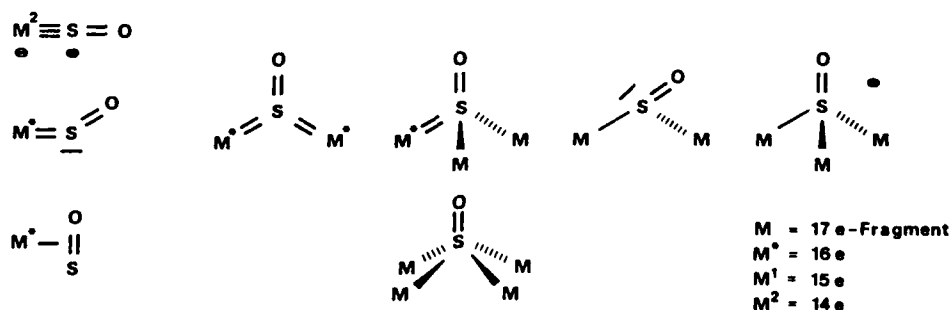
Ingo-Peter Lorenz

Institute for Inorganic Chemistry, University of Tübingen  
Auf der Morgenstelle 18, D-7400 T ü b i n g e n (FRG)

Sulfur monoxide is extremely unstable, but it can be stabilized as ligand in organometallic complexes where it is inserted by different methods of synthesis:

1. directed S-oxidation of metal-coordinated sulfur.
2. SO-transfer reaction by metal-induced fragmentation of thiirane-S-oxide acting as SO-source.
3. nucleophilic substitution reaction at the sulfur atom of thionylchloride by hydrido complexes/amines.

Sulfur monoxide demonstrates a great structural variety as a ligand in organometallic complexes, depending on the number of electrons of the complex fragment, thus, SO can act as 2 or 4 electron donor in terminal or bridging ligand positions:



Starting from suitable organometallic compounds we succeeded in the synthesis of some examples of most of the bonding systems introduced above, which are isolobal analogues of sulfur dioxide, sulfur trioxide, sulfoxides and sulfones.

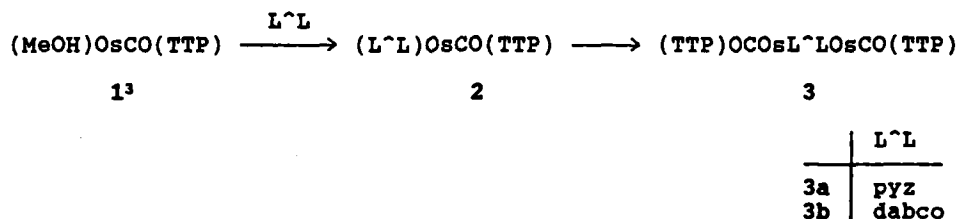
Hitherto, the SO ligand shows four different reaction modes:

1. Substitution of SO against CO ligands
2. Oxidation of SO into SO<sub>2</sub> ligands
3. Insertion of SO<sub>2</sub> into the S-O-bond to give thiosulfato ligands
4. Deoxygenation of SO to sulfur ligand (by HCl)

# BINUCLEAR CARBONYLOSMIUM PORPHYRINS WITH BRIDGING NITROGEN DONOR LIGANDS

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Osmium porphyrins, e. g.  $[\text{Os}(\text{OEP})]_2^{1+}$ , may serve as building blocks for the synthesis of conductive polymers in which bidentate nitrogen donors  $\text{L}^-\text{L}$ , e. g. pyrazine (pyz) or 1,4-diazabicyclo[2,2,2]octane (dabco), are used as bridging donor ligands.<sup>2</sup> The polymers of the type  $[\text{Os}(\text{OEP})(\text{L}^-\text{L})]_n$  are highly conductive when doped, i. e. partially oxidized. The defect electrons appear to be delocalized along the  $\dots\text{Os}(\text{L}^-\text{L})\text{Os}(\text{L}^-\text{L})\dots$  chain. In order to check the presence of  $\text{Os}(\text{L}^-\text{L})\text{Os}$  interactions in isolated molecules, the synthesis of binuclear carbonylosmium(II) porphyrins 3 containing such an entity was undertaken according the sequence 1  $\rightarrow$  2  $\rightarrow$  3.



The species 2 were observed in solution, but lost  $\text{L}^-\text{L}$  on attempted crystallization, thus forming 3a and 3b. The new compounds were characterized by elemental analyses, UV/VIS-, IR-, and  $^1\text{H}$ -NMR spectra. Electrochemical investigations gave no hint of  $\text{OsL}^-\text{LOs}$  coupling in the oxidized forms of 3, 3a<sup>+</sup> or 3b<sup>+</sup>.

- (1)  $(\text{OEP})^{2-}$ ,  $(\text{TTP})^{2-}$ : dianions of octaethylporphyrin or tetra(p-tolyl)porphyrin, respectively.
- (2) J. P. Collman, J. T. McDewitt, C. R. Leidner, G. T. Yee, J. B. Torrance, and W. A. Little, *J. Am. Chem. Soc.* 109, 4606 (1987).
- (3) J. W. Buchler, G. Herget, and K. Oesten, *Liebigs Ann. Chem.* 1983, 2164.

EQUILIBRIUM AND KINETIC STUDY OF IMIDAZOLE BINDING TO  
 PHTHALOCYANINATOIRON(II) IN DIMETHYL SULPHOXIDE

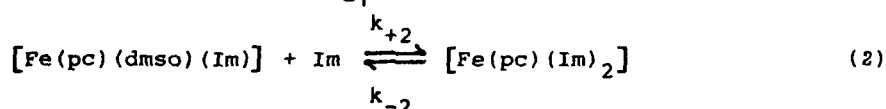
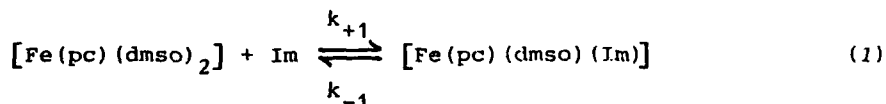
Paolo Ascenzi e Maurizio Brunori, Dipartimento di Scienze Biochimiche, Università di Roma "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy

Giovanna Pennesi, Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione, Area della Ricerca del C.N.R., Via Salaria Km. 29,5, C.P. 10, 00016 Monterotondo Stazione (Roma), Italy

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Ligand binding to phthalocyaninatoiron(II),  $[\text{Fe}(\text{pc})]$ , a porphyrin-like molecule, has been widely investigated from both equilibrium and thermodynamic viewpoints (1).

As a development of our research on this field, we looked at imidazole, Im, as an interesting axial ligand, and since conflicting results were present in the literature (1), a reinvestigation of the reversible reactions (1) and (2) in dimethyl sulphoxide, dmsO,



from both equilibrium and kinetic points of view, seemed necessary. At 20°C, the equilibrium constants are  $K_1 = k_{+1}/k_{-1} = (6.4 \pm 2.6) \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ , and  $K_2 = k_{+2}/k_{-2} = (7.4 \pm 0.5) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ . Values of  $k_{+1}$  and  $k_{+2}$  are  $(9.8 \pm 0.2) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $5.4 \pm 0.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. From these parameters, values of  $k_{-1} = 1.5 \times 10^{-2} \text{ s}^{-1}$  and  $k_{-2} = 7.3 \times 10^{-4} \text{ s}^{-1}$  were calculated. These results show that the replacement of axial dmsO in  $[\text{Fe}(\text{pc})(\text{dmsO})_2]$  by Im is a two-step process with the uptake of the second Im molecule slower than the first.

- (1) F.H. Moser and A.L. Thomas, 'The Phthalocyanines', CRC Press, Boca Raton, 1983.

REACTIONS OF DOUBLY REDUCED IRON(II) PORPHYRINS WITH  
(n, SEC, AND TERT) ALKYL HALIDES.

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Jussieu 75 251 Paris Cedex 05 -France.

Electrochemical investigation of the reduction of seven iron porphyrins (the octaethylporphyrin, the etioporphyrin I, the pentafluorotetraphenylporphyrin, the tetraphenylporphyrin and three basket-handle porphyrins) in the presence of (n, sec. and tert.) alkyl halides shows that not only the singly reduced iron(II) complex, formally and iron(I) complex, undergoes alkylation at the atom, but that this is also the case for the doubly reduced iron(II) complex. No ring alkylation, as possible with a radical anion or a di-anion structure, is observed. At low concentrations of alkyl halide, the one-electron reduction product of the iron(II) alkyl complex, formally and iron(I) alkyl complex, could be transiently observed. Upon raising the concentration, catalytic reduction of the alkyl halide by the  $\text{Fe(II)R}^-/\text{Fe(I)R}^{2-}$  couple occurs. It is found that the presence of the amide linked chains exerts a pronounced influence on the electrochemical and chemical reactivity of the alkyl complexes, stabilizing the negatively charged species. Implications concerning the alkylation mechanisms and the chemical catalysis of the electrochemical reduction of alkyl halides by metal complexes are discussed.

References :

- Lexa D., Savéant J.M., Wang D.L. Organometallics 1986, 5, 1428.  
Lexa D., Savéant J.M., Su K.B., Wang D.L., J.Am.Chem.Soc. (submitted)  
Gueutin C., Lexa D., J.M. Savéant, Wang D.L., Inorg.Chem. (submitted)

SYNTHETIC STRATEGIES TO TRANSITION METALS CORROLATES.  
CRYSTAL AND MOLECULAR STRUCTURE OF (TRIPHENYLARSINE) OCTAMETHYL-  
CORROLATE RHODIUM (III).

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The synthesis of transition metal corrolates has been widely investigated in order to ascertain the possible consequences of the macrocyclic ring deformation (a direct bond between pyrroles A and D) on its coordination properties.

Three main synthetic methods have been so far used to prepare metallocorrolates:

- a) Reaction of the preformed macrocycle with metal carbonyls in a non coordinating solvent.
- b) Reaction of metal salts with the linear tetrapyrrolic intermediate 1,19-dideoxybiladiene-a,c in a buffered alcoholic solution. The presence of a coordinating ligand has proved to be necessary when the metal is rhodium.
- c) Reaction of metal salts with the macrocycle in N,N-dimethylformamide.

The reactivity towards axial ligand, such as phosphines, arsines or isocyanides has also been investigated and an X-ray crystal structure determination has been performed on (triphenylarsine)octamethylcorrolate rhodium (III).

The compound crystallizes in the orthorhombic space group  $P2_12_12_1$  with  $a = 20.172(7)$ ,  $b = 12.468(5)$ ,  $c = 14.893(5)$  Å and  $Z = 4$ . The structure was solved by conventional Patterson and Fourier methods and refined by least-squares procedures to a conventional R value of 0.0353 for 1436 independent reflections collected by counter methods.

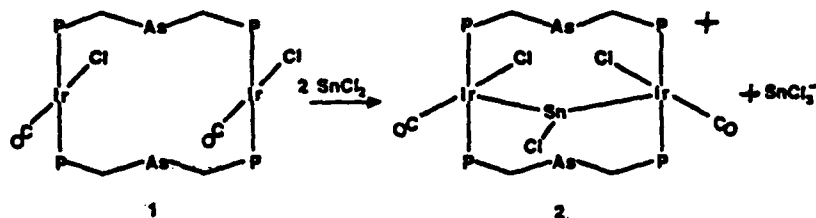
The crystal structure consists of discrete monomeric units, where the rhodium atom has a distorted square pyramidal environment, the equatorial sites being occupied by four nitrogen from the corrole ligand (Rh-N 1.93(1) - 1.96(1) Å) and the apex by the arsenic atom from the triphenylarsine molecule (Rh-As 2.311(2) Å). The 15 atom core of the corrole moiety is nearly planar, the largest deviation from the plane of best fit being 0.10 Å.

NOVEL CHEMICAL BEHAVIOR OF THE METALLOMACROCYCLES  $\text{Ir}_2(\text{CO})_2\text{Cl}_2\{(\text{Ph}_2\text{PCH}_2)_2\text{AsPh}\}_2$ :

BINDING OF MAIN GROUP IONS PARTICULARLY  $\text{Sn}(\text{II})$ .

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The iridium metallomacrocycle  $\text{Ir}_2(\text{CO})_2\text{Cl}_2\{(\text{Ph}_2\text{PCH}_2)_2\text{AsPh}\}_2$  binds a variety of metal ions from both the transition series and the main group elements. This presentation will focus on the interactions with tin(II) which is summarized in eq. 1. The X-ray crystal structure of 2a will be compared to that of related transition metal counterparts. The metallomacrocycle 1 is capable of extracting tin selectively (in the presence of certain other metal ions) from aqueous solution and is capable of transporting tin through a non-aqueous medium. The adduct 2 shows a prominent absorption in the visible spectrum at 588 nm. In solution at 25°C, strong emission at 645 nm is observed. A molecular orbital model for the bonding within this unit will be presented. Removal of tin(II) from 2 is possible and a novel light-driven system for tin(II) extrusion will be described.



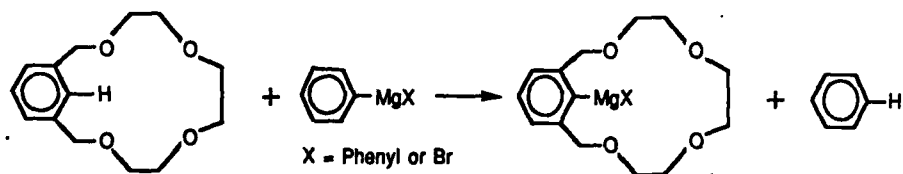
# METALLATION OF AN AROMATIC C-H BOND BY CROWN ETHER ACTIVATED ORGANOMAGNESIUM COMPOUNDS

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de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

During a study on intra- and intermolecular complexation in organomagnesium compounds we found that diphenylmagnesium and 1,3-xylyl-18-crown-5 form a 1:1 complex which can be crystallized from toluene. The X-ray structure analysis revealed a "threaded" or rotaxane structure.

For reasons of structural comparison, the analogous complex with 1,3-xylyl-15-crown-4 was also prepared. Surprisingly, the X-ray structure of the crystalline material showed that an asymmetric, crown ether ring containing, diphenylmagnesium had been formed. The  $^1\text{H}$  NMR spectrum of the precursor in  $[\text{D}_8]\text{toluene}$  showed the relatively slow formation of benzene.

The crown ethers mentioned also form complexes with phenylmagnesium bromide. The 1,3-xylyl-18-crown-5 formed a 1:1 complex with the Grignard compound of which the crystal structure was determined. However, the complex with the 1,3-xylyl-15-crown-4 decomposed under the formation of benzene and a crown ether containing a Grignard function:



These remarkable metallation reactions of the aromatic C-H bond, normally known only for organolithium compounds, must result from the increased reactivity of the magnesium compounds through complexation with the crown ether system. We suggest that the marked difference in behaviour between the crown-5 and crown-4 complexes is due to the much more congested structure of the, intermediately formed, crown-4 complexes in which the aromatic C-H bonds in the 2-position are forced into the very close vicinity of the magnesium centre.

The metallation reactions proceed quantitatively and are believed to be favoured by the stronger co-ordination of magnesium in the products.

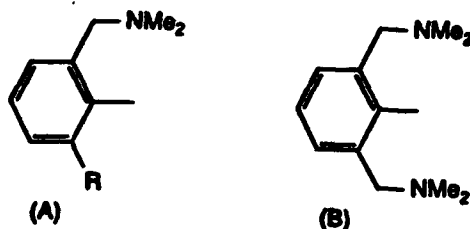
The mechanism of the complex formation and of the subsequent decomposition reactions will be discussed as well as the crystal structures of the complexes and of the magnesium compounds formed in the metallation reactions.



## TUNING THE REACTIVITY OF METALS HELD IN A RIGID LIGAND ENVIRONMENT

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In our studies we have found that specific chelating ligands afford metal complex substrates that are ideally suited for investigating intermediate species formed in reactions with electrophiles. An overview of some of our results in this area using square-planar  $d^8$   $Ni^{II}$ ,  $Pd^{II}$ ,  $Pt^{II}$ ,  $Rh^I$ , and  $Ir^I$  substrates, and the unique organometallic species we encountered are presented. Research in our laboratory has been focussed on the chemistry of monoanionic aryl ligands having *ortho*- or bis-*ortho* dimethylaminomethyl substituents (i.e.  $[C_6H_4(CH_2NMe_2)-2]$  (A) and  $[C_6H_3(CH_2NMe_2)_2-2,6]$  (B)) that form organometallic compounds with a direct M-C<sub>aryl</sub>  $\sigma$ -bond.



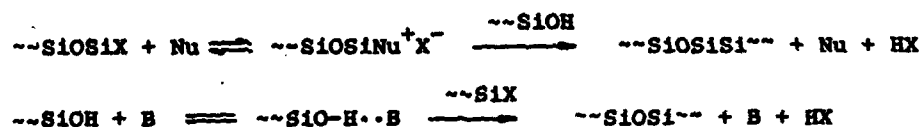
Through coordination of the N donor site(s) of the *ortho*  $CH_2NMe_2$  arm(s) five-membered M-C-C-C-N chelate ring formation occurs. In most cases, this intramolecular coordination hampers decomposition *via* pathways involving M-C bond breaking processes such as homolytic and heterolytic fission. In particular, the rigid chelating coordination of the aryl ligand B, provides the metal centre with a set of unusual properties. Firstly, the bis-*ortho* chelating ligand restricts the available sites for incoming reagents and other ligands. This is a situation that, as we will see, can frustrate the normal course of, for example, an oxidative reaction and lead to "trapped" intermediates having considerable stability. Secondly, the hard C and N donor atom(s) increase the nucleophilicity of the metal centre. This destabilizes the  $d_{z^2}$  orbital that lies perpendicular to the coordination plane in the square planar metal  $d^8$  complexes derived from the ligands A and B. As a consequence, these complexes become susceptible to attack by a variety of electrophiles such as  $H_2$ , MeI, halogen and  $Me_2SnBr_2$ , - with startling results. An example of the unexpected and novel properties of these complexes is the use of organonickel II and III complexes derived from the bis-*ortho* chelating ligand B, for the addition of polyhalogenalkenes to alkene double bonds in homogeneous catalysis.

BASE-NUCLEOPHILE CATALYSIS OF POLYCONDENSATION  
OF FUNCTIONAL SILOXANES

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The heteropolycondensation of functional siloxane oligomers seems to be the most convenient route to many siloxane polymers and copolymers of regular structure. However, in many cases the reaction is slow and accompanied by siloxane bond cleavage as well as by other side processes. We found that using of basic or nucleophilic species, such as amines, phosphine oxides and others, is very effective in this reaction. Kinetics of the reaction of model compounds was studied and the mechanism of the catalysis was elucidated. In the case of strong nucleophiles, such as DMAP, Imidazole or *N*-methylimidazole, the process involves transient formation of a complex of the nucleophile with the polymer end group. At least some of these complexes have ionic structure, e.g. of an ammonium or phosphonium salt. In the case of relatively strong bases, such as  $\text{Et}_3\text{N}$ , the mechanism of base catalysis is more probable, involving activation of silanol group through hydrogen bonding with amine.



Kinetic evidence for both mechanisms will be presented.

THE CHEMICAL DISPLACEMENT OF Os(II) CARBONYL SURFACE SPECIES  
ANCHORED TO HYDROXYLATED SILICA.

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The thermal decomposition of  $\text{HOs}_2(\text{CO})_{10}(\text{OSi})_2$  produces new Os(II) surface species characterized by three infrared carbonyl bands at 2126, 2038 and 1956  $\text{cm}^{-1}$  (1). The real structure of these surface organometallic species still remains an open question. The formation of either mononuclear sites, or dimeric and polymeric  $[\text{Os}(\text{CO})_2]_n$  and  $[\text{Os}(\text{CO})_2]_n$  units without metal-metal bonds has been reported (2).

The chemical displacement of these surface species is performed through the complete disaggregation of the silica with aqueous hydrofluoric acid (3). No osmium carbonyl species is recovered from the aqueous phase by extraction with either  $\text{CH}_2\text{Cl}_2$  or  $\text{PPN}^+ \text{Cl}^-$  in  $\text{CH}_2\text{Cl}_2$ .

The solution was then evaporated at 70°C and a dark residue was obtained. Its infrared spectrum, in a KBr matrix, in the  $\nu\text{CO}$  region presents the same three carbonyl band pattern of the starting supported species. The presence of coordinated water and hydroxo groups is suggested by several  $\delta(\text{OH})$ ,  $\delta(\text{OH}_2)$  and  $\nu(\text{OH})$  vibrations, in addition to the expected  $\delta(\text{Os}-\text{C}-\text{O})$ ,  $\nu(\text{OsC})$ ,  $\delta(\text{O}-\text{Os}-\text{O})$  bands.

A preliminary investigation with E.I. mass spectrometry shows an ion at 592 m/z, whose predominant fragmentation involves the successive loss of four carbon monoxide units has been observed.

A dimeric  $\text{Os}_2(\text{CO})_4(\mu-\text{O})_2(\text{OH}_2)_4$  structure could be tentatively suggested.

1. R. Psaro, R. Ugo, G.M. Zanderighi, B. Besson, A.K. Smith and J.M. Basset, *J. Organomet. Chem.*, 213 (1981) 215.
2. S.L. Cook, J. Evans, G.S. McNulty, G.N. Greaves, *J. Chem. Soc. Dalton Trans.*, (1986) 7.
3. C. Dossi, R. Psaro, R. Zanonì and F.S. Stone, *Spect. Acta*, 43 A (1987) 1507.

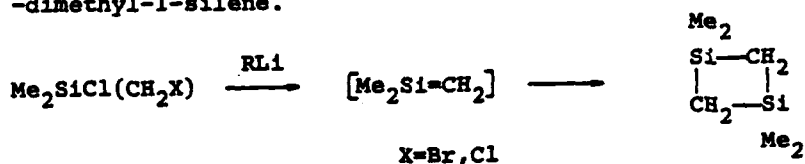
METHODS FOR PREPARATION OF  
1,1,3,3-TETRAMETHYL-1,3-DISILACYCLOBUTANE

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of Sciences, Boczna 5, 90-362 Łódź, Poland

There is a growing interest in preceramic polymers, which consist a useful source for silicon carbide ceramics. Ring opening polymerization of 1,3-disilacyclobutanes can give preceramic polycarbosilanes.

The studies of effective synthetic methods, in solution, leading to 1,1,3,3-tetramethyl-1,3-disilacyclobutane were performed, involving reactions of bromo- and chloromethyl(dimethyl)chlorosilane with organolithium reagents. The reactions show the features of an addition-elimination process, proceeding via unstable 1,1-dimethyl-1-silene.



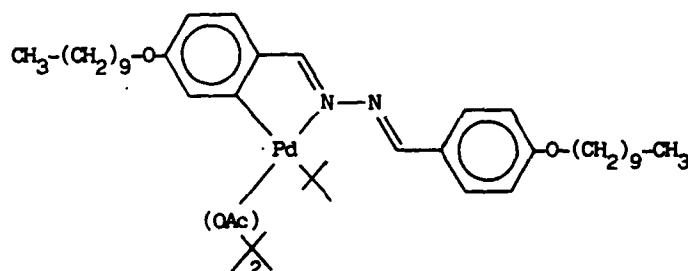
**LIQUID CRYSTALS DERIVED FROM ORTHOPALLADATED-AZINE DIMERS:  
THE INFLUENCE OF THE BRIDGING GROUP.**

P. Espinet and J. Pérez, Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid (Spain).

M. Marcos, B. Ros and J.L. Serrano, Química Orgánica, Facultad de Ciencias, I.C.M.A. Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza (Spain).

E. Lalinde, Química Inorgánica, Colegio Universitario de la Rioja, Universidad de Zaragoza, Logroño (Spain).

Orthometallation of the azine  $p\text{-C}_{10}\text{H}_{21}\text{-O-C}_6\text{H}_4\text{-CH=N-N=CH-C}_6\text{H}_4\text{-OC}_{10}\text{H}_{21}\text{-p}$  with palladium acetate produces reasonable yields of the product orthopalladated in only one of the two rings of the azine,



In spite of the fact that carboxylate groups induce an open-book shape in the molecule that is expected to disturb the mesogenic properties, yet the molecule displays liquid-crystal behaviour.

Related complexes where the acetate group has been replaced by other increasingly larger carboxylate groups (up to 14 C atoms) reveal a surprising influence of the increasing length in the carboxylate chains, leading first to a decrease and then to a recovery of mesogenic properties, when the chain is sufficiently large.

The mesogenic properties of the compounds have been studied by optical microscopy and differential scanning calorimetry and the type of mesophase has been assigned.

CATALYTIC POLYMERIZATION OF ETHYLENE WITH  
(BISCYCLOPENTADIENYL COMPLEXES+ALUMOXANS) SYSTEMS

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Instituto Superior Técnico, Av. Rovisco Pais - 1096 Lisboa-CODEX  
Portugal

Peter Tait, Department of Chemistry, University of Manchester  
Institute of Science and Technology, Manchester M60 1QD, UK.

The subject of this work is ethylene polymerization using  
Kaminsky Type catalysts:  $\text{Cp}_2\text{MR}_2$ +alumoxan.

$\text{M}=\text{Zr}, \text{Mo}, \text{W}$ ;  $\text{R}=\text{Cl}, \text{CH}_3$  (1,2).

The catalytic activity of complexes  $\text{Cp}_2\text{WCl}_2$ ,  $\text{Cp}_2\text{Mo}(\text{CH}_3)_2\text{PF}_6$   
is compared with that of  $\text{Cp}_2\text{ZrCl}_2$ . As expected the activity of the  
Mo and W complexes is smaller than the activity of the Zr complex.

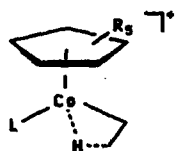
In this communication we report active centers determination by  
quench method with tritium methanol (3), and kinetic studies of  
( $\text{Cp}_2\text{WCl}_2$ +methylalumoxan) system.

- (1) - Jens Herving and Walter Kaminsky, Polymer Bulletin, 9, 464  
(1983)
- (2) - W. Kaminsky, Massoud Miri, H. Sinn and R. Woldt, Makromol.  
Chem., Rapid Commun., 4, 417 (1983)
- (3) - D.R. Burfield and P.J.T. Tait, Polymer, Vol 13, July 315  
(1972)

STRUCTURE AND DYNAMICS OF Co(III) AND Rh(III)  
ETHYLENE HYDRIDE COMPLEXES. MIGRATORY INSERTION  
REACTIONS AND POLYMERIZATION

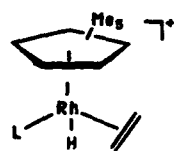
D. Lincoln, A. Volpe, and M. Brookhart, Department of Chemistry,  
Campus Box 3290, The University of North Carolina at Chapel Hill,  
Chapel Hill, North Carolina 27599-3290, U.S.A.

The structure, spectroscopic properties and dynamics of complexes of **1** and **2** will be reported. The mechanism of ethylene polymerization of certain compounds in this series will be described together with preliminary results regarding methods for



**1**

L = C<sub>2</sub>H<sub>4</sub>, PMe<sub>3</sub>,  
P(OMe)<sub>3</sub>, PPh<sub>3</sub>  
R = H, CH<sub>3</sub>



**2**

L = PMe<sub>3</sub>, P(OMe)<sub>3</sub>,  
P(OPh)<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>

preparing terminally functionalized oligomers and polymers of ethylene.

ANALYTICAL ELECTRON MICROSCOPY OF LARGE TRANSITION METAL  
CARBONYL CLUSTERS AND CLUSTER DERIVED CATALYSTS

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Analytical Electron Microscopy studies of large transition metal carbonyl clusters have been carried out on a Phillips 400em machine using electron energy loss spectroscopy (EELS) and X-ray energy dispersive analysis (EDA). Previous studies showed that the cluster  $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{42}]^{5-}$  was deposited intact on a carbon film support and EELS analysis showed Ni:C:O ratios which are consistent with those expected for this anion. Degradation of the cluster was observed with time and electron beam intensity to give a Ni/Pt alloy. Similar studies have now been carried out on other clusters and the order of stability to electron beam damage is  $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{42}]^{5-} < [\text{Pt}_{38}(\text{CO})_{44}\text{Hx}]^{2-} < [\text{Ni}_{34}\text{C}_4(\text{CO})_{38}]^{6-}$ .<sup>3</sup> Efforts are being made to characterise the new materials left after CO evolution and results on these materials will be reported.

Analytical techniques have also been used to study the bimetallic cluster  $\text{Fe}_2\text{Pd}_2(\text{CO})_5(\text{NO})_2(\text{dppm})_2$  used as a catalyst for the reductive carbonylation of nitro derivatives to iso-cyanates.<sup>4</sup> Results from studies before and after catalysis show that metal segregation occurs during catalysis to give particles (200 -500 Å) which are either pure Pd or pure Fe.

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STUDIES INTO THE STEREOSELECTIVITY OF REDUCTION OF CYCLIC KETONES  
WITH ALUMINIUM COMPOUNDS SUPERIMPOSED ON THE ADSORBENT SURFACE

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In search for new reducing agents we have come to investigations of stereoselectivity of reduction of cyclic ketones with aluminium compounds as  $\text{LiAlH}_4$ ,  $(1-\text{C}_4\text{H}_9)_2\text{AlH}$ ,  $(1-\text{C}_4\text{H}_9)_3\text{Al}$ ,  $(1-\text{C}_4\text{H}_9)_2\text{AlH}\cdot\text{ZnCl}_2$  fixed on the surface silica gel, aluminium oxide, and Florisil. 3-Methylcyclohexanone (3MCH), menthone, and camphor have been taken as model compounds. Our investigation results are given in Table 1.

TABLE 1

Reagent	menthone				camphor		3-MCH	
	men- tol	neo- men- tol	bor- neol	iso- bor- neol			cis-	trans-
$\text{LiAlH}_4$	74	26	8	92			84	16
$\text{LiAlH}_4\cdot\text{SiO}_2$	38	62	13	87				
$(1-\text{C}_4\text{H}_9)_2\text{AlH}$	46	54						
$(1-\text{C}_4\text{H}_9)_2\text{AlH}\cdot\text{SiO}_2$	34	66	6	94			70	30
$(1-\text{C}_4\text{H}_9)_2\text{AlH}\cdot\text{ZnCl}_2$	21	79						
$[(1-\text{C}_4\text{H}_9)_2\text{AlH}\cdot\text{ZnCl}_2]\cdot\text{SiO}_2$	0	100						
$(1-\text{C}_4\text{H}_9)_3\text{Al}$	8	92	4	96			47	53
$(1-\text{C}_4\text{H}_9)_3\text{Al}\cdot\text{SiO}_2$	0	100	1	99			56	44
* $(1-\text{C}_4\text{H}_9)_3\text{Al}\cdot\text{Al}_2\text{O}_3$	8	92						
$(1-\text{C}_4\text{H}_9)_3\text{Al}\cdot\text{Florisil}$	0	100	0	100			53	47

Solvent - ether, \*-hexane

The results presented demonstrate the applicability of aluminium reagents superimposed on the adsorbent to improve the stereoselectivity of reduction of hindered cyclic ketones to the related alcohols of lower thermodynamic stability.

A NEW CARBONYL CLUSTER SYSTEM. SYNTHESIS AND MOLECULAR STRUCTURES  
OF  $[\text{Ni}_{12}\text{Ge}(\text{CO})_{22}]^{2-}$  AND  $[\text{Ni}_{10}\text{Ge}(\text{CO})_{20}]^{2-}$  DIANIONS.

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The new Ni-Ge carbonyl cluster system has been investigated. The reaction of  $[\text{Ni}_6(\text{CO})_{12}]^{2-}$  (I) with  $\text{GeCl}_4$  in acetonitrile solution ( $\text{GeCl}_4$ /(I) ca. 0.6 as molar ratio) affords the  $[\text{Ni}_{12}\text{Ge}(\text{CO})_{22}]^{2-}$  (II) dianion ( $\nu(\text{CO})$  in THF: 2020(s), 1835(m), 1775(mw), brown soln.); when the reaction is performed with a higher molar ratio (ca. 2.5) another compound, viz.  $[\text{Ni}_{10}\text{Ge}(\text{CO})_{20}]^{2-}$  (III) ( $\nu(\text{CO})$  in THF: 2010(s), 1975(m), 1865(ms), 1845(m), green soln.) is obtained.

The direct degradation of (II) into (III) results with excess  $\text{GeCl}_4$ , however an analogous transformation can be achieved on using either CO or  $\text{PPh}_3$  as degradation agents.

Crystals of (II) and (III) as  $\text{PPh}_4^+$  salts have been prepared by slow diffusion of isopropylalcohol in THF solution. Their molecular structures, determined by X-ray diffraction analysis, are based on a Ge-centered icosahedral packing of metal atoms. The metal skeleton of (III) is directly obtained from that of (II) by removing two opposite Ni atoms. The only reported analogous structures in carbonyl cluster family are those of  $[\text{Ni}_{12}\text{Sn}(\text{CO})_{22}]^{2-}$  (1) and of  $[\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}$  (2).

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**BRIDGED CYANO-SUBSTITUTED BUTA-1,3-DIENYLIDENE  
AND CYCLOPENTYLIDENE DIIRON COMPLEXES.**

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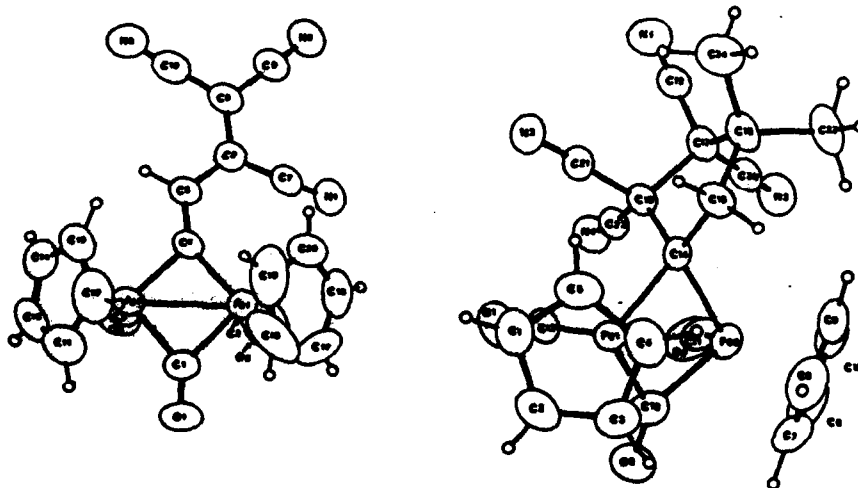
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Tetracyanoethylene (TCNE) is a widely used reagent in several kinds of organic reactions. Some of these have proven to be subtly different in transition-metal chemistry. On the other hand, bridging alkenylidene diiron complexes can be viewed as 1,1-dimetallated olefins, an important feature of their potential use in organic synthesis and model reactions.

The reaction of the  $\mu$ -alkenylidene diiron complexes  $[(C_5H_5)Fe(CO)]_2(\mu-CO)(\mu-C=CHR)$  ( $R = H, CH_3$ ) with TCNE gives the  $\mu$ -3,4,4-tricyanobuta-1,3-dienylidene compounds  $[(C_5H_5)Fe(CO)]_2(\mu-CO)[\mu-C=CR-(NC)C\equiv C(CN)_2]$  ( $R = H, CH_3$ ), resulting from the tricyanovinilation of the ligand. The  $\mu$ -buta-1,3-dienylidene ligand is rare and relevant spectroscopic data together with the X-ray structure of one complex ( $R = H$ ) are presented.

When TCNE reacts with the isopropyl substituted complex  $[(C_5H_5)Fe(CO)]_2(\mu-CO)[\mu-C=CHCH(CH_3)_2]$ , a [1,2] hydrogen shift occurs leading to an unexpected  $\mu$ -cyclopentylidene complex  $[(C_5H_5)Fe(CO)]_2(\mu-CO)[\mu-C-CH_2-C(CH_3)_2-C\equiv C(CN)_2]$  whose X-ray structure has been determined.

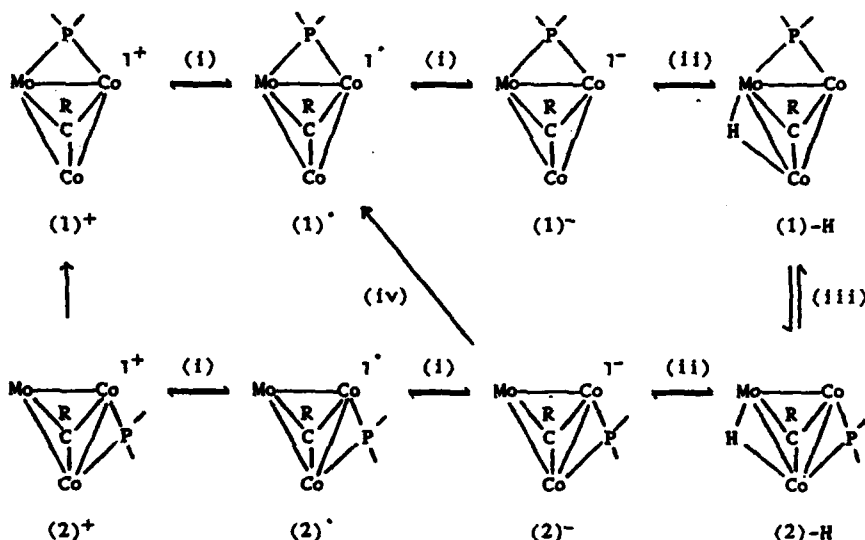
Preliminary mechanistic results will be provided.



# The Synthesis, Reactivity and Redox Properties of Phosphido-bridged Clusters

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We are currently examining the synthesis and properties of series of related organometallic clusters in order to identify redox induced cluster activation reactions with organic or inorganic substrates. The phosphido-bridged complexes under investigation are typically prepared *via* controlled addition of either  $\text{PPh}_2\text{H}$  or  $\text{LiPPh}_2$  to appropriate neutral precursors such as  $[\text{MoCo}_2(\mu_3\text{-CR})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ .<sup>1-4</sup> Some reactions of phosphido-clusters derived from the latter complex are shown below:



Peripheral ligands omitted for clarity. (i)  $\pm 1e$ , (ii)  $\pm 2H^+$ , (iii) isomerises under ambient conditions, (iv)  $-1e$ , isomerisation may proceed *via* (2), (2)<sup>•</sup>, and (1)<sup>•</sup>.

Chemical and electrochemical studies suggest the existence of a complex series of isomeric cationic, radical, anionic and neutral hydride species. We have identified novel redox induced phosphido-bridge isomerisation of (2)<sup>-</sup> to (1)<sup>•</sup> and can also isolate closely related kinetic and thermodynamic isomers [eg. (1)<sup>-</sup> and (2)<sup>-</sup>]. Clusters of the types shown appear to be accessible for a wide variety of metal-ligand combinations and potentially have a rich and diverse chemistry. Thus treatment of (1)<sup>•</sup> with  $[\text{W}=\text{CR}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  gives initially a tetrametal radical which subsequently fragments to give good yields of the dimetal radical  $[\text{MoCo}(\mu\text{-(RC=CR)})(\mu\text{-PR}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ . Controlled cluster expansion may also be achieved, thus (2)<sup>-</sup>H with  $[\text{Rh}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  sequentially affords the new tetra- and penta-nuclear clusters  $[\text{MoCo}_2\text{Rh}(\mu_3\text{-CR})(\mu\text{-CO})_2(\mu\text{-PR}_2)(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  and  $[\text{MoCoRh}_2(\mu_3\text{-CR})(\mu_2\text{-CO})(\mu\text{-CO})_2(\mu\text{-PR}_2)_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)]$ .

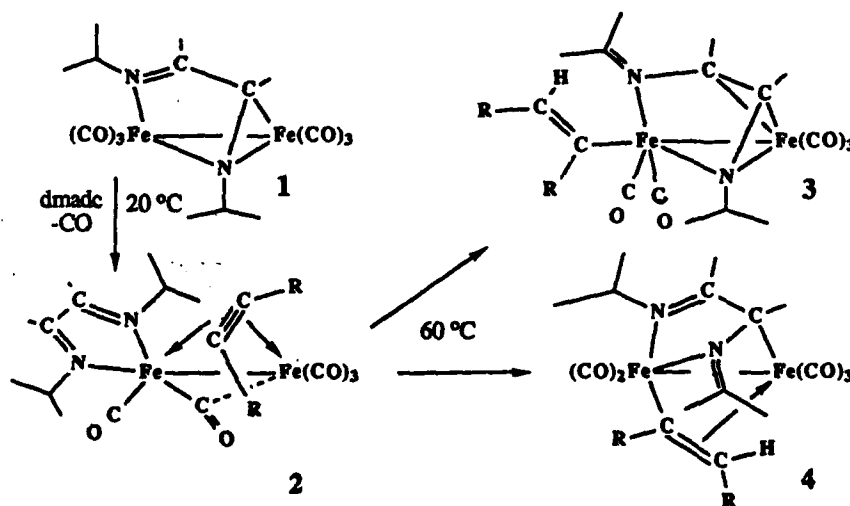
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# UNUSUAL HYDROGEN MIGRATIONS FROM AN $\alpha$ -DIIMINE LIGAND TO A COORDINATED ALKYNE ON A DIIRON CARBONYL COMPLEX

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$\text{Fe}_2(\text{CO})_6(\text{iPr-DAB})$  (1) [ $\text{iPr-DAB} = \text{iPr-N}=\text{CHCH}=\text{N-iPr}$ ], with a  $\sigma\text{-N}, \mu_2\text{-N}', \eta^2\text{-C}=\text{N}'$  bridging 6e donating  $\alpha$ -diimine ligand, reacts with  $\text{MeOC(O)C}\equiv\text{CC(O)OMe}$  (dmadc) to give  $\text{Fe}_2(\text{CO})_5(\sigma\text{-N}, \sigma\text{-N}', \mu_2\text{-iPr-DAB})(\mu_2, \eta^2\text{-dmadc})$  (2) (X-ray) with a chelating DAB ligand and a perpendicular bridging alkyne. Its formation proceeds via the substitution of the  $\eta^2\text{-C}=\text{N}$  bonded imine moiety in 1 by an  $\eta^2\text{-C}\equiv\text{C}$  bonded alkyne, followed by the loss of one CO ligand. Complex 2 shows a remarkable thermally induced rearrangement involving the migration of one of the DAB iPr methine protons to the coordinated alkyne, resulting in the formation of two isomeric products 3 and 4. In  $\text{Fe}_2(\text{CO})_5[\eta^1\text{-MeOC(O)C}=\text{CHC(O)OMe}][\text{Me}_2\text{C}=\text{N-CHCHN-iPr}]$  (3) (X-ray) the alkyne is transformed into a monodentate bonded vinyl fragment and the DAB into a  $\sigma\text{-N-imino-}\eta^3\text{-aza-allyl}$  ligand. In the other isomer,  $\text{Fe}_2(\text{CO})_5[\mu_2, \eta^2\text{-MeOC(O)C}=\text{CHC(O)OMe}][\text{iPr-N}=\text{CHCH-N}=\text{CMe}_2]$  (4) the vinyl ligand is bridging both metal centers. The formation of the two different isomers probably originates from the reaction of the alkyne with the two different i-Pr methine protons in 2. The proton transfer most likely proceeds directly from the DAB to the alkyne and does not involve a metal-hydride intermediate. These results show that not only  $\eta^2\text{-C}=\text{N}$  coordinated imine fragments, but also chelate bonded DAB ligands are activated towards reactions with alkynes.



**CRYSTAL STRUCTURES OF SEVERAL TRIOSMIUM CLUSTERS AND  
THE GEOMETRIES OF CALCULATED HYDRIDE POSITIONS IN THESE CLUSTERS.**

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The crystal and molecular structures of several triosmium clusters as well as clusters containing two trimetal-cluster rings connected by the  $[\text{CH}\equiv\text{CCO}]^-$  ligand are presented. Examples are  $\text{HOs}(\text{CO})_6(\text{O}_2\text{C}_2\text{H})$ ,  $\text{H Os}_2(\text{CO})_{19}(\text{O}_2\text{C}_2)$  and  $\text{HRu}_3\text{Os}_3(\text{CO})_{20}(\text{O}_2\text{C}_2\text{H})$ . The mode of attachment of the acetylenic end of the ligand to the triosmium unit is examined as well and the overall geometry of the molecule.

The program HYDEX by Guy Orphen at Bristol University has been used to calculate bridging hydride positions in the above mentioned binuclear clusters as well as in numerous other triosmium cluster molecules. The X-ray structures of several compounds are presented along with an examination of the hydride positions calculated using HYDEX versus the hydride positions predicted from a consideration of the geometry of the ligands around the metal atoms in the cluster.

## ELECTROCHEMICAL BEHAVIOUR OF SOME ORGANOMETAL-CLUSTERS

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The electrochemistry of transition metal clusters represents one of the most recent aspects of their characterization and a good test for their catalytic activity in reactions involving redox sequences. In binary metal carbonyls, the HOMO and LUMO are generally metal-metal bonding and anti-bonding in character, respectively, thus the anodic oxidation and the cathodic reduction cause quick and irreversible cluster degradation.

The coordination to the metallic frame of a large organic chain, able to clasp several metal atoms together and to improve the electronic delocalization over the entire molecule, increases the life-times of the electrogenerated ionic species when compared with parent clusters / 1-3 /. So, organometal-clusters often exhibit electrochemical and chemical reversibility and formal redox potentials can be evaluated ; consequently, electronic and thermodynamic information can be obtained making use of free-energy correlations.

The electrochemical behaviour of two series of organometal-clusters, namely  $M_3(CO)_8(Alkyne)_2$  ( $M=Fe, Ru$ ) and  $Fe_2(CO)_6(Butatriene)$  will be discussed along with the related electron-transfer catalyzed ( ETC ) reactions.

Work supported by European Economic Community.

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REDUCTION OF THE PHOSPHORUS-BRIDGING CARBONYL GROUP  
IN CARBONYLBIS(DIISOPROPYLAMINOPHOSPHIDO)HEXACARBONYLDIIRON

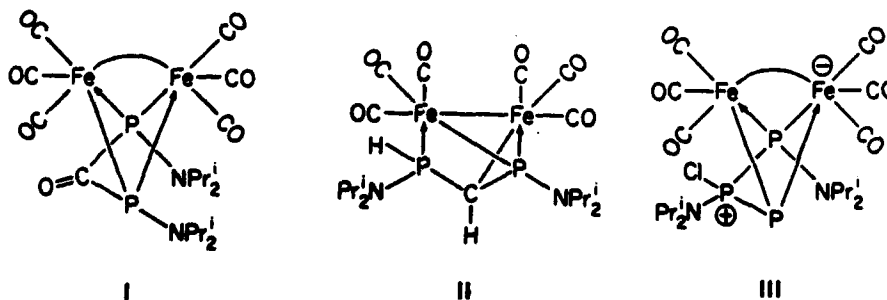
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Reaction of  $\text{iPr}_2\text{NPCl}_2$  with  $\text{Na}_2\text{Fe}(\text{CO})_4$  in diethyl ether solution results in migration of a carbonyl group from iron to phosphorus to give the phosphorus-bridging carbonyl complex  $(\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  (I) in ~35% yield thereby making this air-stable complex readily available in ~40 gram quantities. This complex can be regarded as a novel analogue of a ketone in which the carbonyl group is bonded to two phosphorus atoms rather than two carbon atoms. This paper summarizes studies on the reduction of the phosphorus-bridging carbonyl group in this complex with diverse reducing agents.

Treatment of  $(\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with  $\text{NaBH}_4$  in methanol results in reduction of the phosphorus-bridging carbonyl group to give the corresponding secondary alcohol  $(\text{iPr}_2\text{NP})_2\text{CHOHFe}_2(\text{CO})_6$ . Similar treatment of  $(\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with  $\text{LiAlH}_4$  in diethyl ether results in more extensive reduction to give a product of stoichiometry  $(\text{iPr}_2\text{NP})_2\text{CH}_2\text{Fe}_2(\text{CO})_6$  shown, however, by X-ray diffraction to be  $(\text{iPr}_2\text{NPCHPHNIPr}_2)\text{Fe}_2(\text{CO})_6$  (II) in which an iron-phosphorus bond has been broken and a new iron-carbon bond formed. Treatment of  $(\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with the alkylolithiums  $\text{RLi}$  ( $\text{R}=\text{Me}$ ,  $\text{nBu}$ ) results in addition to the phosphorus-bridging carbonyl group to give the corresponding tertiary alcohols  $(\text{iPr}_2\text{NP})_2\text{C}(\text{R}(\text{OH}))\text{Fe}_2(\text{CO})_6$ . Reduction of  $(\text{iPr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$  with sodium amalgam in tetrahydrofuran results in cleavage of a diisopropylamino group to give the anion  $[(\text{iPr}_2\text{NPCOPFe}_2(\text{CO})_6)]^-$  which can be isolated as its orange bis(triphenylphosphine)iminium salt or as the light orange trimethyltin derivative  $(\text{iPr}_2\text{N})(\text{Me}_3\text{Sn})\text{P}_2\text{COFe}_2(\text{CO})_6$ . Reaction of  $[(\text{iPr}_2\text{NPCOPFe}_2(\text{CO})_6)]^-$  with  $\text{iPr}_2\text{NPCl}_2$  results in rearrangement with expulsion of the phosphorus-bridging carbonyl group to give orange  $[(\text{iPr}_2\text{NP})(\text{iPr}_2\text{N})(\text{Cl})\text{PP}]\text{Fe}_2(\text{CO})_6$  shown by X-ray diffraction to have a structure III with a triphosphorus chain bridging a  $\text{Fe}_2(\text{CO})_6$  unit through the end phosphorus atoms. One of the end phosphorus atoms of this triphosphorus chain is an ordinary diisopropylaminophosphido group whereas the other end phosphorus atom is trigonal pyramidal with a lone pair. The center atom of this triphosphorus chain is four-coordinate being bonded to the other two phosphorus atoms, a diisopropylamino group, and a chlorine atom.





# ACTIVATION OF PHENYLACETYLENE IN COMPLEXES WITH $\text{Re}_2$ AND $\text{Re}_2\text{Mo}_2$ FRAMEWORK

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Alkyn-containing complexes of transition metals are of interest as the model systems allowing to study the mechanism of the formation of catalytically active intermediates in heterogeneous catalysis on the molecular level.

By the direct synthesis from  $\text{Re}_2(\text{CO})_{10}$  and  $\text{HC CPh}$  at UV radiation in ether hydride acetylenide complex  $\text{Re}_2(\text{CO})_8(\mu\text{-H})(\mu\text{-C}\equiv\text{CPh})$  (I) was obtained which is an intermediate in rearrangement of phenylacetylene complexes. Regeneration of  $\text{HC}\equiv\text{CPh}$  as its complex with heterometallic cluster takes place in the reaction of complex I with  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  in boiling o-xylene during the first five-six hours. X-Ray structural analysis has shown that the resulting cluster  $\text{Cp}_2\text{Mo}_2\text{Re}_2(\text{CO})_8(\mu\text{-CO})_2(\mu^4, \eta^2\text{-PhC}\equiv\text{CH})$  (II) contains a heterometallic framework "butterfly"  $\text{Re}_2\text{Mo}_2$  with a dihedral angle  $110,7^\circ$ . Bond  $\text{C}\equiv\text{C}$  of phenylacetylene ligand is coordinated by the type  $\mu^4, \eta^2$  and is extended ( $1,47(2)\text{\AA}$ ) unlike noncoordinated  $\text{C}\equiv\text{C}$  bond ( $1,22(1)\text{\AA}$ ) and it is situated parallel the bond  $\text{Mo}^1\text{-Re}^2$ . The presence of hydrogen in molecule  $\text{PhC}\equiv\text{CH}$  is proved by the singlet in  $^1\text{H-NMR}$  spectrum in weak fields ( $\delta$  11,83 a.f. relative TMS).

At the further running of the reaction (10-11 hours) the transformation of complex II to heterometallic cluster  $\text{Cp}_2\text{Re}_2\text{Mo}_2(\mu\text{-H})(\text{CO})_7(\mu\text{-CO})(\mu^4, \eta^4, \eta^1\text{-C}\equiv\text{C})(\mu, \eta^1, \eta^2\text{-Ph})$  (III) takes place. In cluster III the separation of hydrogen from phenylacetylene ligand and coordination of acetylenide according to  $\sigma\text{-}\pi$  type are observed. III also contains heterometallic framework "butterfly"  $\text{Re}_2\text{Mo}_2$  with dihedral angle  $119,5^\circ$ , the length of bond  $\text{C}\equiv\text{C}$  of phenylacetylenide ligand is  $1,48(1)\text{\AA}$ . Electron-unsaturated cluster III (60 electrons) is an intermediate; in its coordination sphere the introduction of small molecules is possible.

VIBRATIONAL SPECTRA AND STRUCTURES OF  
BIS(ETHENE)TETRACARBONYL COMPLEXES  
OF MOLYBDENUM AND TUNGSTEN.

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The stable bis(ethene) complexes,  $(C_2H_4)_2M(CO)_4$ , where  $M = Cr, Mo$  or  $W$ , have recently been synthesised.[1] As part of a study of the vibrational spectra of transition-metal ethene complexes, e.g. [2,3], we now report on the infrared and Raman spectra of the complexes with  $M = Mo$  or  $W$ , both as solids and as solutions in hexane and liquid xenon.

Almost complete vibrational assignments have been obtained for both complexes. The results show that 'local symmetry' approximation is not valid for the  $M(CO)_4$  units, and that the molecules maintain  $D_{2h}$  symmetry in solution.

The vibrational assignments for the ethene fragment show that there is very little coupling between the two  $C_2H_4$  units, and that a  $(C_2H_4)_2M$  model of  $C_{2v}$  symmetry is adequate. The predominantly C=C stretching mode is at  $1185cm^{-1}$  ( $M = W$ ) or  $1210cm^{-1}$  ( $M = Mo$ ). The  $M-(C_2H_4)$  stretching modes, however, reveal that some vibrational coupling does occur in the skeletal modes; the totally symmetric  $W-C_2H_4$  stretch, for example, appears as a doublet ( $333, 369\ cm^{-1}$ ), due to in-phase and out-of-phase motions of the  $(C_2H_4)_2-W-(C_2H_4)$  unit.

Force field calculations for the  $M-C_2H_4$  fragment for  $M = Mo(0), W(0), Fe(0), Pt(0)$  and  $Pt(II)$  suggest that the M-C bond strength is in the sequence  $W(0) > Mo(0) > Pt(II) > Fe(0) > Pt(0)$ . Similar calculations for the  $M(CO)_4$  units ( $M = Mo$  or  $W$ ), and comparison with the parent hexacarbonyls give useful information on the relative bonding abilities of  $C_2H_4$  and  $CO$ .

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SYNTHESIS AND REACTIVITY OF THE COMPLEXES  $[\text{MCp}_2(\text{SR})(\text{NCR}')][\text{PF}_6]$   
(M=Mo(IV); W(IV); R=aryl or alkyl, R'=aryl derivative)

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Previously we have described the chemical oxidation of the complexes  $[\text{MCp}_2(\text{SR})_2]$  (M=Mo(IV), W(IV); R=alkyl or aryl) with ferricinium cation in the presence of nucleophiles (1). In this communication, we report the synthesis of several nitriles derivatives,  $[\text{MCp}_2(\text{SR})(\text{NCR}')][\text{PF}_6]$  (R'=aryl substituted) by the same method.

In order to infer on the  $\pi$  delocalization of the nitrile attached to the organometallic moiety, we present the results of proton magnetic resonance spectra and compare with free ligands. Also we report the results of these compounds by cyclic voltammetry and study their chemical and electrochemical reactivity.

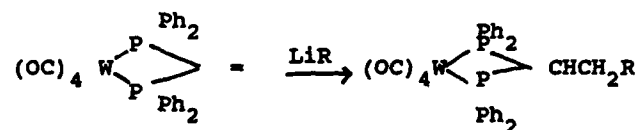
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J. Organomet. Chem., 320, 63-81 (1987).

SYNTHESIS OF FUNCTIONALIZED DIPHOSPHINE-W(CO)<sub>4</sub> COMPLEXES  
VIA CARBANION ADDITIONS

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Treatment of complexes of the type  $[W(CO)_4((Ph_2P)_2C = CH_2)]$  with functionalized lithium reagents,  $LiR$ , followed by hydrolysis gives complexes of the type  $[W(CO)_4(Ph_2P)_2CHCH_2R]$  in high yields;  $R = C_6H_4OMe-2$ ,  $C_6H_3(OMe)_2-2.6$ ,  $C_6H_4OH-2$ ,  $C_6H_4(COOH)-2$ ,  $CH_2COPh$  or  $CH_2COMe$ . This result is particularly interesting because addition reaction of functionalized carbanion to vinylene complexes gives a new novel possibility to synthesize functionalized phosphines which would be difficult to make in other ways. Vinylidene diphosphine  $(Ph_2P)_2C = CH_2$  itself is relatively inert towards Michael conjugate addition, but becomes activated while complexed to metal (1,2). Details of the synthesis are discussed.



$R = C_6H_4OMe-2$ ,  $C_6H_3(OMe)_2$ ,  $C_6H_4OH-2$ ,  $C_6H_4(COOH)-2$ ,  $CH_2COPh$ ,  $CH_2COMe$

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P-C(sp<sup>3</sup>) BOND CLEAVAGE LEADING TO A VERY REACTIVE  
UNSATURATED DIMOLYBDENUM CARBONYL COMPLEX.

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During decarbonylation and hydrogenation experiments on dppm-bridged dimanganese and dimolybdenum carbonyl complexes (dppm:Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>), we have found that carbon-phosphorous (P-CH<sub>2</sub>) bond cleavage is a relevant process operative under relatively mild conditions (70 - 110°C). For example, heating [MoCp(CO)<sub>2</sub>]<sub>2</sub>(μ-dppm) 1, (Cp:η-C<sub>5</sub>H<sub>5</sub>) <sup>(1)</sup> in thf at 70°C for 30 min. yields [Mo<sub>2</sub>(μ-CH<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)Cp<sub>2</sub>(CO)<sub>2</sub>]<sub>2</sub> 2 in c.a. 65% yield. While the resulting diphosphine cleavage process leading to 2 strongly parallels that one found in [Fe<sub>2</sub>(CO)<sub>7</sub>(μ-R<sub>2</sub>PCH<sub>2</sub>PR<sub>2</sub>)] species <sup>(2)</sup>, an even more interesting feature in 2 arises from its insaturation (Mo=Mo, on the basis of electron counting), which should markedly increase the synthetic potential of this type of species.

Compound 2 readily reacts with H<sub>2</sub> or CO at r.t.; in the CO reaction, the complex [Mo<sub>2</sub>(μ-CH<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(CO)<sub>3</sub>Cp<sub>2</sub>]<sub>2</sub> 3 is isolated, in which the Mo-Mo bond order has been reduced to one. On the other hand, compound 2 can be protonated and it also reacts with oxidizing agents such as NO<sup>+</sup>, FeCp<sub>2</sub><sup>+</sup> or I<sub>2</sub>; in the latter reaction, a two electron oxidation leads to the dication [Mo<sub>2</sub>(μ-CH<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)Cp<sub>2</sub>(CO)<sub>2</sub>]<sub>2</sub><sup>2+</sup> 4, which formally contains a triple molybdenum-molybdenum bond.

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SYNTHESIS AND CHARACTERIZATION OF TETRANUCLEAR HYDROXO CARBONYL  
COMPLEXES,  $[\text{Et}_4\text{N}]_4[\text{M}(\text{CO})_3(\mu_3\text{-OH})]_4$  (M = Mo, W)

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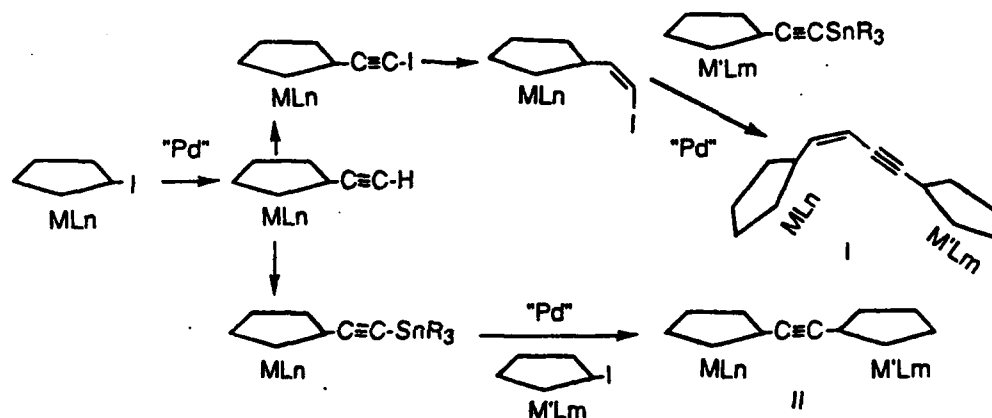
Reaction of  $\text{M}(\text{CO})_3(\text{PMTA})$  (M = Mo, W; PMTA = 1,1,4,7,7-Pentamethyldiethylenetriamine) With tetraethylammonium hydroxide in aqueous THF solution provides  $[\text{Et}_4\text{N}]_4[\text{M}(\text{CO})_3(\mu_3\text{-OH})]_4$  (1, M = Mo; 2, M = W). The crystal structures of both complexes have been determined. Compounds 1 and 2 are iso-structural; the crystals are monoclinic, space group  $\text{C2/C}$ ,  $Z = 4$ , with unit cell dimensions  $a = 23.888(7)$ ,  $b = 12.3000(2)$ ,  $c = 23.254(3)$  Å,  $\beta = 123.85(2)^\circ$  for 1 and  $a = 23.86(3)$ ,  $b = 12.317(7)$ ,  $c = 23.21(1)$  Å,  $\beta = 123.8(2)^\circ$  for 2. The anions consist of a distorted  $\text{A}_4\text{B}_4$  (A = metal, B = oxygen) core with triply bridging hydroxide groups and  $\text{M}(\text{CO})_3$  units. The characterization and reactivity of these species will be described. Noble derivatives of 1 and 2,  $(\text{Ph}_3\text{PAu})_4\text{M}_4(\text{CO})_{12}(\text{OH})_4$  (M = Mo, W), were isolated in good yields.

## SYNTHESIS OF HETEROBIMETALLIC CLUSTERS

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By using the palladium-catalyzed cross-coupling reaction between trialkyltinacetylide and aromatic or vinylic iodide<sup>1</sup>, we developed two general routes for the formation of heterobimetallic clusters of the formula I and II:



In our hands, we found that the nature of M and M' can range between groups 4 and 8, allowing a wide variety of combinations. The only requirement for a given metal to be introduced in the synthetic route is the availability of its  $\eta^5$ -iodocyclopentadienyl derivative. Since it can be obtained by metallation/iodination of the corresponding cyclopentadienyl derivative<sup>2</sup>, by treatment of cyclopentadienyl diazide with iodometal derivative<sup>3</sup> or by treatment of the metal halide with  $\eta^5$ -iodocyclopentadienyl thallium<sup>4</sup>, the possibilities in the combination of M and M' are enormous.

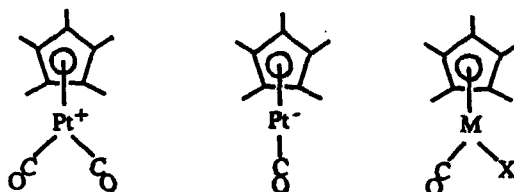
Structures I and II are promising for the investigation of CO reduction by homogeneous catalysis because of the possible cooperative effect of M and M' during the catalytic cycle.

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# PENTAMETHYLCYCOPENTADIENYL COMPLEXES OF PLATINUM AND PALLADIUM

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We have recently devised high yield syntheses of  $[\text{Pt}_2(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)_2]$  **1**  
and  $[\text{Pd}_2(\mu\text{-CO})_2(\eta^5\text{-C}_5\text{Me}_5)_2]$  **2** and converted them into to key precursors  
 $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]^+$ , **3**,  $[\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})]^-$ , **4**, and  $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{X}]$   
(**5**,  $\text{M} = \text{Pd}$ ,  $\text{X} = \text{I}$ ; **6**,  $\text{M} = \text{Pt}$ ,  $\text{X} = \text{I, Br, Cl}$ ).



$\text{M} = \text{Pd}, \text{X} = \text{I}$ , **5**  
 $\text{Pt}, \text{X} = \text{I}$ , **6a**  
 $\text{Br}$ , **6b**  
 $\text{Cl}$ , **6c**

We will discuss the physical and chemical properties of complexes **3-6** and discuss  
typical and atypical chemistry we find to be associated with complexes of these types.



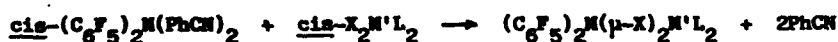
# SYNTHESIS OF ASYMMETRIC BINUCLEAR PENTAFLUOROPHENYL DERIVATIVES OF THE NICKEL GROUP ELEMENTS

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The synthesis of neutral binuclear organo-complexes  $R_2M(\mu-X)_2M'L_2$  in which the metal atoms have different coordination environments requires the availability of a labile organometallic complex,  $R_2ML'_2$ , that can react with a halo-complex,  $M'X_2L_2$ , to give the desired product. Complexes of the type  $(C_6F_5)_2ML'_2$ , where  $L' =$  dioxane,<sup>1</sup> tetrahydrofuran<sup>2</sup> or benzonitrile<sup>3</sup> should be good precursors for this purpose.

When the benzonitrile complex  $cis-M(C_6F_5)_2(PhCN)_2$  ( $M = Ni, Pd, Pt$ ) and the appropriate halo-complex  $M'X_2L_2$  ( $M' = Ni, Pd, Pt$ ;  $X = Cl, Br, I$ ;  $L =$  mono- or bidentate phosphine) are allowed to react in dichloromethane the corresponding homo- or hetero-bimetallic complexes are formed according to the following equation:



The new compounds have been characterized by microanalyses and IR,  $^{19}F$ - and  $^{31}P$ -NMR spectroscopies. The  $^{31}P$  resonances are clearly influenced by the coordination of  $X_2M'L_2$  to the  $R_2M$  moiety.

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## A NEW VIEW OF THE FISCHER-TROPSCH POLYMERISATION REACTION

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Recent results on model complexes will be presented which are leading to a new view of the mechanism of the Fischer-Tropsch polymerisation reaction.

Vinyl Complexes of Ruthenium(II): Intermediates in Reductive Elimination, Ring Closure and Catalytic Reactions

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Complexes  $[\text{Ru}(\text{CO})_2\text{XYL}_2]$  ( $\text{L} = \text{PMe}_2\text{Ph}$  or  $\text{AsMe}_2\text{Ph}$ ,  $\text{X} = \text{Y} = \text{H}$ ,  $\text{Me}$  or  $\text{Cl}$ ;  $\text{X} = \text{H}$ ,  $\text{Y} = \text{Cl}$ ;  $\text{X} = \text{aryl}$ ,  $\text{Y} = \text{Cl}$ ) react with activated alkynes such as  $\text{MeO}_2\text{C}\equiv\text{CCO}_2\text{Me}$  to yield vinyl complexes  $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{X}\}\text{YL}_2]$ . Where  $\text{X} \neq \text{Y}$ , insertion occurs preferentially in an  $\text{Ru-H}$  bond, and least readily in  $\text{Ru-Cl}$ . Hydride complexes  $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{X}\}\text{HL}_2]$  exist in solution as pairs of conformers, and slowly rearrange to alkene complexes  $[\text{Ru}(\text{CO})_2\{\text{CH}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{X}\}\text{L}_2]$ . The compounds  $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})(\text{C}_6\text{H}_4\text{Z-4})\}\text{ClL}_2]$  are formed in a single isomeric form, yet they undergo ring closure at 323 K to give both  $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})(\text{C}_6\text{H}_3\text{Z-4})\}\text{L}_2]$  and  $[\text{Ru}(\text{CO})_2\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2)(\text{C}_6\text{H}_4\text{Z-4})\}\text{L}_2]$ , by  $\text{HCl}$  and  $\text{MeCl}$  elimination respectively, implying ready interconversion of isomers of the vinyl complexes.

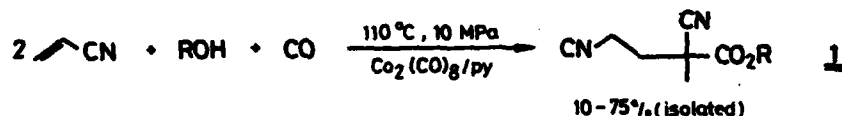
The ease and reversibility of the transfer of organic ligands between mercury and ruthenium are nicely illustrated by our discovery of a catalytic cycle, using  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$ , for converting diaryl mercury compounds  $[\text{Hg}(\text{C}_6\text{H}_4\text{Z-4})_2]$  to new vinyl compounds  $[\text{Hg}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})(\text{C}_6\text{H}_4\text{Z-4})\}(\text{C}_6\text{H}_4\text{Z-4})]$  and  $[\text{Hg}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})(\text{C}_6\text{H}_4\text{Z-4})\}_2]$ . Transfer of an aryl ligand from mercury to ruthenium is followed by alkyne insertion on ruthenium and then by return of the vinyl ligand to mercury.

COBALT CARBONYL MEDIATED MICHAEL ADDITION. DIRECT SYNTHESIS  
OF DICYANO ESTERS FROM ACRYLONITRILE

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The hydrocarbalkoxylation of acrylonitrile with stoichiometric amounts of alcohols in the presence of  $\text{Co}_2(\text{CO})_8$ /pyridine catalyst leads directly to 2,4-dicyano-2-methyl-butanoic acid esters<sup>1</sup>:



The yield of 1 increases at the expense of two cyanopropionic acid ester byproducts,  $\text{NCCH}(\text{CH}_3)\text{CO}_2\text{R}$  and  $\text{NCCH}_2\text{CH}_2\text{CO}_2\text{R}$  (c.f. ref 2), with the increasing relative concentration of pyridine, and it has a maximum at  $[\text{py}]/[\text{Co}] \approx 2$ . Secondary alcohols give the best yields. Model reactions proved, that the catalytic cycle starts with the addition of  $\text{pyH}[\text{Co}(\text{CO})_4]$  on acrylonitrile giving the alkyl complex  $\text{NCCH}(\text{Me})\text{Co}(\text{CO})_4$  (2). 2 leads to the byproducts through isomerization and/or carbonylation (c.f. ref 3), however, it could be also deprotonated by pyridine to a "Michael-donor" anion  $\text{NC}\bar{\text{C}}(\text{Me})\text{Co}(\text{CO})_4$ , which reacts with acrylonitrile giving 1 after all.

Analogous reactions using equimolar amounts of alcohol, acrylonitrile and an other activated olefin lead to products with at least 3 different functional groups.

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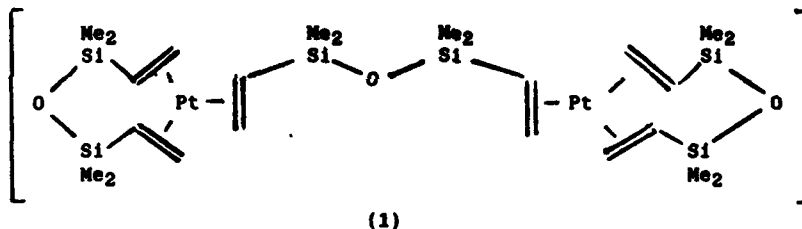
Pt(0) AND Rh(I) HYDROSILYLATION CATALYSTS CONTAINING  
CHELATING AND/OR BRIDGING DIVINYLDISILOXANES

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Nicholas J.W. Warhurst

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Brighton, U.K.

It has recently been shown by Chandra, Lo, Hitchcock, and Lappert that the hydrosilylation catalyst (solution A), obtained by refluxing  $\text{H}_2[\text{PtCl}_6] \cdot x\text{H}_2\text{O}$  in  $(\text{ViSiMe}_2)_2\text{O}$ , is a Pt(0) species, from which further Pt(0) complexes may be isolated.<sup>1</sup>

We shall show that solution A comprises a mixture of two diastereoisomers (variable temperature  $^{195}\text{Pt}$ ,  $^{29}\text{Si}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ , and  $2\text{D-}^1\text{H}$  COSY n.m.r. spectroscopy). The crystalline complex isolated from A was a single (rac) diastereoisomer (1) (X-ray data), also obtained from  $[\text{Pt}(\text{cod})_2]$  and  $(\text{ViSiMe}_2)_2\text{O}$ .



A crystalline Rh(I) complex,  $[\text{Rh}(\eta\text{-ViSiMe}_2)_2\text{O}](\mu\text{-Cl})_2$  (2) (X-ray data) was obtained from  $[(\text{Rh}(\eta\text{-C}_6\text{H}_{14})_2(\mu\text{-Cl}))_2]$  and  $(\text{ViSiMe}_2)_2\text{O}$ ; (2) was not accessible directly from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and the divinyldisiloxane.

We shall report extensions of this chemistry, including results of investigations of (a) the hydrosilylation catalytic activity of (1) and (2); (b) the function of solution (A) or complexes (1) or (2) as a convenient source of further Pt(0) or Rh(I) complexes, such as  $[\text{Pt}(\text{Sn}(\text{NR}_2)_2)_3]$  ( $\text{R} = \text{SiMe}_3$ );<sup>2</sup> (c) the role of  $(\text{ViSiMe}_2)_2\text{O}$  as a reducing agent in noble metal chemistry; and (d) the mechanistic implications of the formation of (1) from  $\text{H}_2[\text{PtCl}_6] \cdot x\text{H}_2\text{O}$  and  $(\text{ViSiMe}_2)_2\text{O}$ .

We thank Dow Corning PLC (Barry) and S.E.R.C. for the award of a CASE studentship to N.J.W.W. and Drs. A.G. Avent, P.Y. Lo, and R.G. Taylor for useful discussions.

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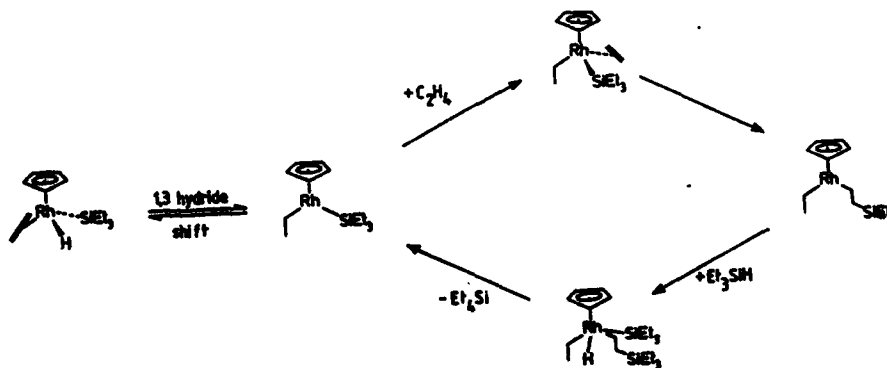
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The Mechanism of Hydrosilation by  $\text{CpRh}(\text{C}_2\text{H}_4)(\text{SiEt}_3)(\text{H})$ 

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Photolysis of  $\text{CpRh}(\text{C}_2\text{H}_4)_2$ , (**1**), ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) in the presence of excess  $\text{Et}_3\text{SiH}$  at 213K yields  $\text{CpRh}(\text{C}_2\text{H}_4)(\text{SiEt}_3)\text{H}$ , **2**, and no hydrosilation products. Similar photolysis of **1** at 300K yields **2**,  $\text{CpRh}(\text{SiEt}_3)_2(\text{H})_2$  (**3**) and hydrosilation products. Isolation of **2** has enabled us to test whether it is directly involved in the catalytic cycle of hydrosilation as would be expected from the Chalk-Harrod mechanism. If **2** is placed under  $\text{C}_2\text{H}_4 + \text{Et}_3\text{SiH}$ , catalytic hydrosilation occurs producing  $\text{Et}_4\text{Si}$ . When  $\text{C}_2\text{D}_4$  is used in place of  $\text{C}_2\text{H}_4$  the main hydrosilation product is  $\text{Et}_3\text{SiCD}_2\text{CD}_2\text{H}$ , but no incorporation of  $\text{C}_2\text{D}_4$  into **2** was observed after four catalytic cycles. Furthermore, reaction of **2** with propene +  $\text{Et}_3\text{SiH}$  gives the corresponding hydrosilation products, but no new Rh products. These results are consistent with the mechanism below in which a 1,3-H shift generates the 16e intermediate  $\text{CpRh}(\text{Et})(\text{SiEt}_3)$  (**4**). In subsequent steps (i)  $\text{C}_2\text{H}_4$  coordinates, (ii) the silyl group migrates onto coordinated ethene and (iii)  $\text{Et}_3\text{SiH}$  adds to form a Rh(V) species (compare **3**), (iv)  $\text{Et}_4\text{Si}$  is eliminated reforming **4**. This mechanism retains the integrity of the  $\text{C}_2\text{H}_4$  group of **2** but does not regenerate **2** in the catalytic cycle.

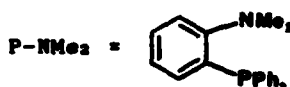
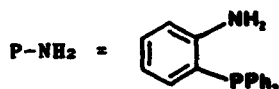


# IRIDIUM COMPLEXES WITH P-N LIGANDS AS CATALYSTS FOR SELECTIVE HYDROGENATION.

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The potentially chelating phosphines P-NH<sub>2</sub> and P-NMe<sub>2</sub> [1] are employed as ligands in the preparation of iridium-based hydrogenation catalysts, starting from [Ir(cod)(OMe)]<sub>2</sub>.



In the presence of such systems, benzylideneacetone is reduced to the corresponding unsaturated alcohol with yields up to 90% when using P-NH<sub>2</sub>. On the basis of <sup>1</sup>H and <sup>31</sup>P NMR data we suggest the catalytically active species to be H<sub>2</sub>Ir(P-NH)(P-NH<sub>2</sub>)<sub>2</sub>, which is formed via N-H oxidative addition to the metal.

The selectivity in carbonyl group reduction could be ascribed to a steric control on the coordination mode of the substrate, which is induced by the presence of three phosphines in the coordination sphere of the iridium atom. Such a steric control of the selectivity has also been suggested in the recently reported hydrogenation of α,β unsaturated carbonyl compounds by H<sub>2</sub>Ir(PR<sub>3</sub>)<sub>3</sub>. [2]

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KEY INTERMEDIATES OF THE RUTHENIUM COMPLEX CATALYZED  
HYDROSILYLATION AND METATHESIS

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Ruthenium chlorophosphine as well as ruthenium chloride based complexes appeared to be novel effective catalysts for hydrosilylation of C=C bonds in alkenes [1,2] and vinylsilanes [2] as well as for metathesis of vinylsubstituted silanes [3]. Some requirements for these reactions e.g. the presence of alkoxy substituents at silicon in hydrosilanes and in vinylsilanes, traces of dioxygen and inhibition by any solvent used, determined the program of ruthenium-silyl intermediate examinations.

A series of reactions of the substrates (triethoxysilane, vinylsilanes) and other ethoxysubstituted silanes (tetraethoxysilane, alkylethoxysilane) with  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  under conditions close to those in the processes studied, allow to isolate ruthenium-silyl complexes characterized by various spectroscopic and other physico-chemical methods. The isolated complexes were subsequently tested in the hydrosilylation of C=C bond and metathesis of vinylsilanes. Complexes prepared under oxygen-free conditions do not show any activity in the hydrosilylation of 1-alkenes, whereas the influence of various factors on ruthenium-carbenes initiation as catalysts for the metathesis is more complex.

The most active isolated complexes provide the basis for mechanistic considerations of the reactions studied.

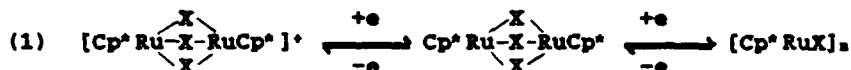
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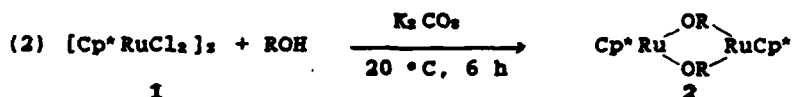
## Stoichiometric and catalytic reactions of Cp\*Ru complexes

U. Koelle, J. Kossakowski and R. Boese<sup>§</sup>Institute of Inorganic Chemistry, Technical University of Aachen,  
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The potential role of complexes Cp\*RuL<sub>2</sub>X<sub>2</sub> as redox catalysts was investigated. A survey of the electrochemical behavior of three groups, i.e. Cp\*RuL<sub>2</sub>X (I), Cp\*RuLX<sub>2</sub> (II) and [Cp\*RuX<sub>2</sub>]<sub>2</sub>, (III) (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>, X = Cl, Br, I) showed group I to give reversible Ru(II/III) electron transfer (E<sub>1/2</sub> ≈ 0 V vs. SCE), whereas the redox behavior of II is complex being associated with loss of X (E<sub>p</sub> ≈ -0.4 V vs. SCE). A two step reversible electron transfer is observed for group III in MeOH (E<sub>1/2</sub> ≈ 0 V vs. SCE) according to eq (1):



[Cp\*RuCl<sub>2</sub>]<sub>2</sub>, 1 acts as an electrocatalyst for alcohol oxidation (e.g. E<sub>1/2</sub> 0.7 V vs. SCE for MeOH). In the presence of a base it is reduced by alcohols in a thermal reaction according to eq (1) giving dinuclear alcoxido complexes 2<sup>1)</sup>.



2a (R = Me) was characterized by single crystal x-ray diffraction as a folded dimer (Ru-Ru 295 pm) with 16-electron-ruthenium. Alcoxido complexes 2 are reactive not only in complexation reactions (3) but also towards acids and oxygen.



Various aspects of the reactions of 2 are discussed.

§) Institute of Inorganic chemistry, University of Essen, D-4300 Essen, G.F.R.; X-ray structure.

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OXIDATION OF ORGANIC SUBSTRATES BY PHOSPHINO-COMPLEXES OF  
RHODIUM, IRIIDIUM, RUTHENIUM AND OSMIUM.

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We report here the preliminary results of an investigation carried out with a number of complexes  $[M(\text{diphos})_2]\text{BF}_4$  (M-Rh, Ir) and  $[\text{MCl}(\text{DPPP})_2]\text{X}$  (M-Ru, Os; DPPP-1,3-bis(diphenylphosphino)propane; X- $\text{PF}_6$ ,  $\text{ClO}_4$ ) using  $\text{LiClO}$  as oxidant of alkenes, alkanes, alcohols and ethers.

In a typical catalytic experiment, a dichloromethane solution containing the complexes (1-2 mM) and the substrate (0.1-1 M) was stirred with an excess of aqueous  $\text{LiClO}$  (0.1-1 M), and aliquots monitored by gas-chromatography. Ruthenium and osmium complexes were stable and active for week-long periods. On the contrary,  $[\text{Ir}(\text{diphos})_2]\text{BF}_4$  rapidly collapsed becoming inactive under these conditions. The related rhodium(I) derivative was instantaneously and quantitatively transformed to a new complex, presumably of rhodium(III), which appears to be the active catalyst.

Secondary alcohols, cyclic and linear ethers were oxidized in high yields to ketones, lactones and esters respectively. Olefins gave epoxides as main products, although in the case of phenyl-substituted alkenes another route was operating which led to products of the oxidative cleavage (benzaldehyde, acetophenone). Under the same conditions, cyclohexane produced small amounts of cyclohexanone.

Work supported by C.N.R. (Centro Stabilità Reattività Composti di Coordinazione) and Ministero Pubblica Istruzione.

## NEW INTERCONVERSIONS IN THE LIGAND SPHERE OF CLUSTERS

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The ability of organometallic clusters to stabilize reactive organic species by multicenter attachment provides the possibility to elucidate bonding modes, stabilities, and reactivities of such species. In this context the following subjects will be addressed:

1. **Synthetic aspects:** reactive tri- and tetranuclear clusters, capping with unsaturated substrates, metal fragment plus substrate assembly reactions.
2. **Reactivity:** rearrangement of multiply bonded substrates, C-C and N-N cleavage, metal attachment and removal, insertion into cluster-C and cluster-H bonds.
3. **Mechanistic aspects:** maintenance of the cluster identity during reactions, fate of substrate fragments, metal-metal versus metal-substrate bond labilities, stereochemistry of reactions involving chiral clusters.

## CHELATING AND BRIDGING BEHAVIOUR OF THE LIGANDS

$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{EPh}_2$  (E = P or As) in  
 $\text{HRu}_3(\text{C}\equiv\text{CBu}^t)(\text{CO})_7(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{EPh}_2)$

ENRICO SAPPA

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Symmetrical or asymmetrical bidentate ligands are useful for stabilizing bimetallic and cluster frames<sup>1</sup> (in view of homogeneous catalytic applications involving reversible metal-metal bond cleavage) or for inducing chirality even in suitable homometallic clusters.<sup>2,3</sup>

We have recently synthesized the chiral cluster  $\text{HRu}_3(\text{C}\equiv\text{CBu}^t)(\text{CO})_7(\text{dppm})$  (dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), which crystallizes as an ordered racemic array of the two enantiomers.<sup>3</sup> The diphosphine dppm, which substitutes two carbonyls in equatorial positions, bridging two ruthenium atoms, blocks the localized CO scrambling processes but promotes a novel fluxional mechanism, inducing the acetylide rotation and the contemporary hydride transfer.

On the other hand, by reacting the parent cluster  $\text{HRu}_3(\text{C}\equiv\text{CBu}^t)(\text{CO})_9$  with the bidentate ligands  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{EPh}_2$  (E = P, dppe; E = As, dppe) in the presence of  $\text{Me}_3\text{NO}$ , we obtained in both cases two isomers of the complexes  $\text{HRu}_3(\text{C}\equiv\text{CBu}^t)(\text{CO})_7(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{EPh}_2)$ , which have been separated by TLC. In the first the ligands chelate the ruthenium atom opposite to the bridging hydride, whereas in the second they bridge a hydride-free edge, as can be deduced from <sup>1</sup>H and <sup>31</sup>P NMR spectra. When dppe behaves as bridging ligand the phosphorus atom is bonded to the ruthenium opposite to the hydride. When chelating, the ligands do not show any fluxional behaviour, when bridging, interconversion between axial and equatorial positions has been observed.

In conclusion, the rather rigid ligand dppm produces only one isomer and promotes acetylide fluxionality, whereas the less sterically demanding ligands dppe and dppe give two isomers and show some mobility.

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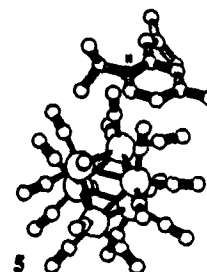
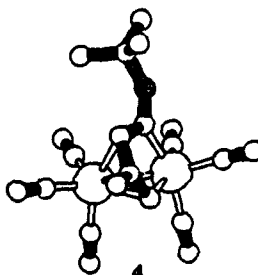
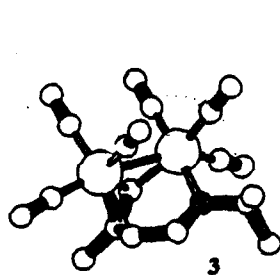
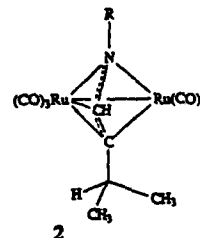
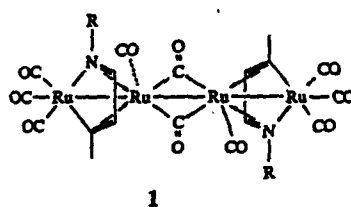
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**Dehydrogenation and coupling of monoazadienes  
on ruthenium carbonyl fragments.**

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The organometallic and coordination chemistry of monoazadienes (which contain the  $N=C-C=C$  moiety) currently receives renewed interest [1,2]. For instance, a new 7 electron coordination mode of the monoazadienyl ligand in the linear tetranuclear complex 1 has recently been described [2]. Compound 1, which can be imagined as an analogue of  $Cp_2Ru_2(CO)_4$ , arises as a major product of the thermal reaction of  $CH_3-CH=CH-CH=NR$  with  $Ru_3(CO)_{12}$  in heptane. Here we report new organoruthenium compounds (2-4) which are formed in reactions of homologs  $(CH_3)_2C=CH-CH=NR$  with  $Ru_3(CO)_{12}$ . Due to the absence of a H-atom at the appropriate position, a metallated product like 1 cannot be formed. Instead, at 85 °C in heptane, azaallylic complex 2 emerges as the result of a 1,2-H shift. At 100 °C also compounds 3 and 4 (X-ray) arise, probably via insertions of Ru into C-H bonds of one methyl group. Furthermore, as a minor product, an intriguing pyridinium complex 5 (X-ray) is found, the organic part of which can overall be viewed as the condensation product of two monoazadienes with net loss of  $RNH_2$ .

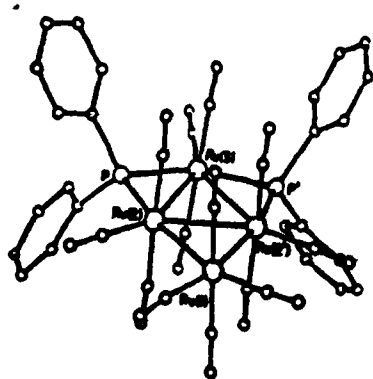


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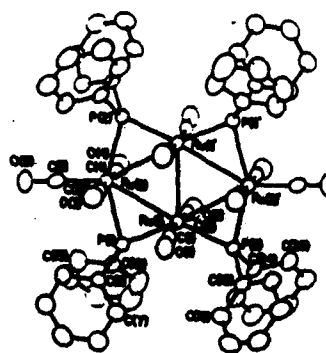
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The Synthesis and Structural Characterisation of a Series of 64- electron Phosphido Stabilised Tetraruthenium Butterfly Clusters. Graeme Hogarth, Jacquie A. Phillips, Nicholas J. Taylor, Todd B. Marder and Arthur J. Carty. Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

Tetranuclear complexes containing a butterfly arrangement of metal atoms are generally characterised by a 62-electron count and contain a folded core, while a 64-electron count is attributed to a square or metalloligated triangular geometry. During the course of our studies on phosphide stabilised clusters we have synthesised a series of 64-electron tetranuclear complexes which contain a planar butterfly framework with elongated ruthenium-ruthenium bonds, namely  $[\text{HRu}_4(\text{CO})_n(\mu\text{-PPh}_2)_m]$  ( $n = 1, 14$ ;  $m = 3, 1$ ) and  $[\text{Ru}_4(\text{CO})_x(\mu\text{-PPh}_2)_y]$  ( $x = 10, 13$ ;  $y = 4, 2$ ). The synthesis, spectroscopic features, structural chemistry and reactivity of these electron-rich clusters typified by (1) and (2) will be described.



(1)



(2)

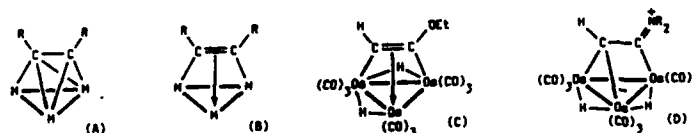
## TRIPLY-BRIDGING FORMS OF PYRROLE AND RELATED LIGANDS IN TRIOSMIUM CLUSTERS

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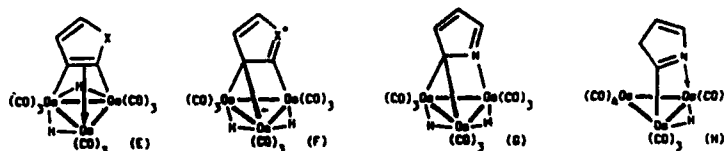
Alejandro J Arce and Ysaora De Sanctis, Chemistry Center, Instituto  
Venezolano Cientificas, Apartado 1827, Caracas 101, Venezuela.

Kenneth I Hardcastle and Michael Day, Department of Chemistry, California  
State University Northridge, Northridge, California 91330, U.S.A.

Triply-bridging alkynes adopt either vertical perpendicular orientations (A) or tilted parallel orientations (B) in trinuclear clusters which may be described as closo or nido respectively in PSEP theory. Thus  $M_3(RC_2R)(CO)_9$  ( $M = Fe, Ru$ , or  $Os$ ) have structure (A) while  $M_3(RC_2R)(CO)_{10}$  or  $M_3H_2(RC_2R)(CO)_9$  ( $M = Ru$  or  $Os$ ) have structure (B).  $\pi$ -Donor substituents  $X$  in  $Os_3H_2(HC_2X)(CO)_9$  can lower the energy of a perpendicular form to make alkyne rotation more rapid as when  $X = OEt$  (C)<sup>1</sup> or even make the perpendicular form the more stable as when  $X = NR_2$  ( $R = H$  or  $Et$ ) (D).<sup>2</sup>



The clusters  $Os_3H_2(C_4H_2X)(CO)_9$  ( $X = S, O, NH$ , or  $NMe$ )<sup>3</sup> containing dehydrogenated forms of thiophene, furan, or pyrrole as ligands adopt the parallel mode (E) (X-ray structures for  $X = S$  or  $NMe$ ) but with some contribution from (F) (greatest when  $X = NMe$ ). When  $X = NH$  the aromatic form (E) readily isomerises to the non-aromatic N-bonded perpendicular form (G). The structure of the non-aromatic derivative of pyrrole  $Os_3H(C_4H_4N)(CO)_{10}$  (H) is also described.



Indole forms analogues of (E) and (H) but the analogue of (G) is inaccessible because the benzo-group would need to span a single bond.

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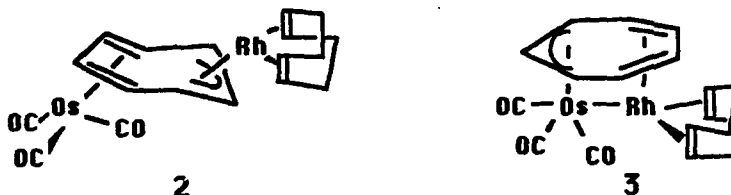
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USE OF  $K^+(C_7H_7)Os(CO)_3^-$  IN THE SYNTHESIS OF  
CYCLOHEPTATRIENYL BRIDGED HETEROBIMETALLIC COMPLEXES

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University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Anionic cycloheptatrienyl complexes of the form  $(C_7H_7)M(CO)_3^-$  ( $M = Fe, Ru, Os$ ) are ideal precursors for the formation of cycloheptatrienyl bridged heterobimetallic complexes upon reaction with unsaturated transition metal halides. We have previously reported on the utility of the Fe and Ru derivatives in this regard.<sup>1,2</sup>

The corresponding anionic osmium complex,  $K^+(C_7H_7)Os(CO)_3^-$  (**1**), has been obtained by deprotonation of  $(\eta^4\text{-cycloheptatriene})Os(CO)_3$  with  $KOtBu$ . **1** reacts with  $[Rh(COD)Cl]_2$  ( $COD = 1,5\text{-cyclooctadiene}$ ) to give **2** as the major product where the two metals straddle the seven membered ring.



The more robust *cis* isomer, **3**, containing a metal-metal bond is a minor product in this reaction. The different bonding of the cycloheptatrienyl ring in the two isomers is clearly seen in the  $^1H$  N.M.R. spectra of the complexes. Whilst at room temperature, ring whizzing is observed for both **2** and **3**, the low temperature limiting spectra for **2** is obtained readily upon cooling.

In an effort to change the reactivity pattern of the anionic osmium complex, the use of alternative deprotonating agents such as butyl lithium is being investigated. Further reactions with other suitable transition metal substrates is also being pursued.

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MULTIPLE CARBON-CARBON BOND CLEAVAGE ON A HEPTAOSMIUM CLUSTER:  
 THE SYNTHESIS AND MOLECULAR STRUCTURE OF  
 $\text{Os}_7(\text{CO})_{18}(\mu_3\text{-CPh})_2$  AND  $\text{Os}_7(\text{CO})_{15}(\mu_3\text{-CPh})_4$

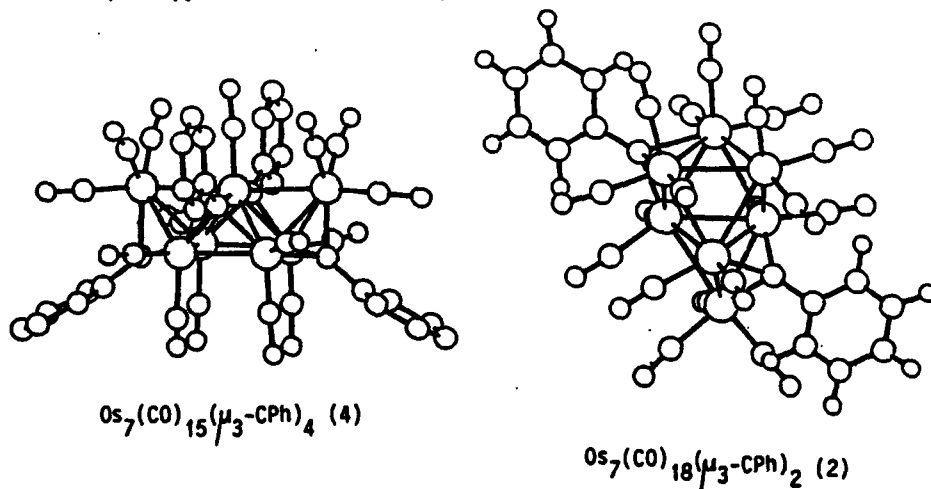
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Brian F. G. Johnson, Jack Lewis, and Julie Lunniss, University Chemical  
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The dihydrido cluster  $\text{H}_2\text{Os}_7(\text{CO})_{20}^1$  (1) reacts with  $\text{Ph}_2\text{C}_2$  in toluene under reflux to initially produce a brown compound (2), then a green compound (3) and finally, after an extended period (~3 days), a purple compound (4). Neither the H n.m.r. nor mass spectral data were particularly informative, save for verifying the presence of phenyl ligands in all three complexes. However, X-ray quality crystals of (2) and (4) could be obtained by slow evaporation of a tetrahydrofuran solution at room temperature.

The X-ray diffraction study identified (2) and (4) as  $\text{Os}_7(\text{CO})_{18}(\mu_3\text{-CPh})_2$  and  $\text{Os}_7(\text{CO})_{15}(\mu_3\text{-CPh})_4$ , respectively. Both species contain three-electron donor  $\mu_3\text{-CPh}$  groups originated by carbon-carbon cleavage of the  $\text{Ph}_2\text{C}_2$  reagent.

It should be emphasized that the  $\mu_3\text{-CPh}$  ligands in (4) supply 12 electrons to the cluster: never before such an extensive electron contribution by ligands other than CO has been observed for Os-clusters. What is more, the starting  $\text{H}_2\text{Os}_7(\text{CO})_{20}$  species undergoes remarkable metal core rearrangements in the course of the reaction yielding two different  $\text{Os}_7$  polyhedra, which share the same electron counting of 98 electrons. It is also noteworthy that the square base of the square pyramid in (4) is unsupported.



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### The Varied Substitution Chemistry of $\text{H}_3\text{BiRu}_3(\text{CO})_9$

Brian F. G. Johnson, Jack Lewis, Paul R. Raithby and Alan J. Whitton.  
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW,  
Great Britain.

The substitution chemistry of the recently reported mixed metal bismuth ruthenium cluster  $\text{H}_3\text{BiRu}_3(\text{CO})_9$  (1,2) is prolific and varied. The three bridging hydride ligands in the parent molecule makes the identification of the products by  $^1\text{H}$  n.m.r. a simple process. This, together with the recent development of a high yield synthetic route to the parent carbonyl, (2) makes this cluster ideally suited to a detailed study of its substitution chemistry, and allows the resolution of isomeric mixtures found in solution.

While it has not been possible as yet to coordinate organic ligands directly to the cluster, the substitution of carbonyl ligands by phosphines, phosphites, arsines, stibines and isocyanides has suggested the existence of 13 of the possible 27 unique structures that can be envisaged for mono-, bis- and tris- substitution of this cluster. In no instance has evidence been obtained which would suggest that greater than one CO per Ru atom has been replaced. We have found that isocyanide ligands have a coordination preference at equatorial sites whilst the more bulky,  $\sigma$ -donor ligands ( $\text{ER}_3$ ; E = P, As, Sb) exhibit an axial preference. Polydentate isocyanide and phosphine ligands have been used to force the cluster into adopting further configurations.

From the results of these experiments we are able to propose a simple model to explain all the observations which is based on the steric interactions of the ligands. Although the steric model encompasses the observation that more than one ligand will not occupy the same metal atom, we believe that the more important reason is that the additional electron density on the substituted Ru atom deactivates the atom towards further CO loss.

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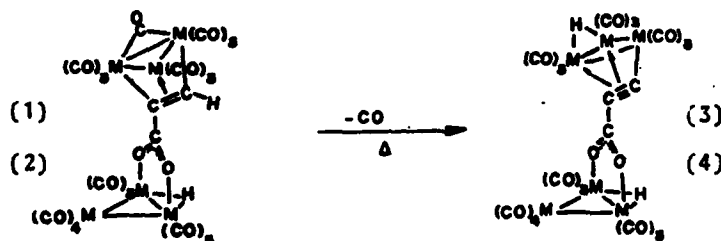
REACTIONS OF ACETYLENIC ALDEHYDES, ETHERS AND  
CARBOXYLIC ACIDS WITH TRIOSMIUM AND TRIRUTHENIUM  
CLUSTERS

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The hydrido cluster  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  reacts with  $\text{CH}\equiv\text{CCHO}$  to give  $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{CH}_2=\text{CCHO})]$  in which the ligand is bridging as a three-electron donor through the oxygen and the unsaturated  $\alpha$ -carbon atoms<sup>1</sup>. On thermolysis, two compounds are formed. One is the isomer  $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{cis-CH}=\text{CHCHO})]$  which has an open structure with two Os-Os bonds, since the organic ligand is now a five-electron donating bridge. The other product is the dinuclear derivative  $[\text{Os}_2\text{H}(\text{CO})_6(\text{cis-CH}=\text{CHCHO})]$ . The clusters  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  and  $[\text{M}_3(\text{CO})_{10}(\text{MeCN})_2]$  ( $\text{M}=\text{Ru}$  or  $\text{Os}$ ) react with  $\text{CH}\equiv\text{CH}_2\text{OMe}$  to give  $[\text{M}_3(\text{CO})_{10}(\text{CH}=\text{CCH}_2\text{OMe})]$  ( $\text{M}=\text{Ru}$  or  $\text{Os}$ ),  $[\text{Os}_3(\text{CO})_9(\text{R-CCHCOCH}=\text{CR})]$  and  $[\text{Os}_3(\text{CO})_9\{(\text{RC}_2\text{H})_2\text{CO}\}]$  ( $\text{R}=\text{CH}_2\text{OMe}$ ), where the last two correspond to alkyne-coupled products.

$[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  and  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  react smoothly with  $\text{CH}\equiv\text{CCO}_2\text{H}$  to give, as expected, the carboxylate derivative  $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{CH}\equiv\text{CCO}_2)]$  which contains an uncoordinated alkyne group<sup>2</sup>. We reacted this compound with  $[\text{M}_3(\text{CO})_{10}(\text{MeCN})_2]$  ( $\text{M}=\text{Ru}$  or  $\text{Os}$ ) to give two new linked clusters in high yields:  $[\text{Os}_6\text{H}(\text{CO})_{20}(\mu^5\text{-CH}\equiv\text{CCO}_2)]$  (1) and  $[\text{Os}_3\text{Ru}_3\text{H}(\text{CO})_{20}(\mu^5\text{-CH}\equiv\text{CCO}_2)]$  (2). Decarbonylation of (1) and (2) affords in quantitative yields the compounds (3) and (4), in which the organic ligand acts as an eight-electron donor system, a remarkable number of electrons for such a small ligand.



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APPLICATIONS OF TWO-DIMENSIONAL NMR SPECTROSCOPY  
TO ORGANOMETALLIC CHEMISTRY

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Organometallic chemistry is frequently associated with complex dynamic molecules. Historically, various NMR methods have been employed to recognize, trace and quantify these rate processes, e.g., line shape analysis and magnetization transfer techniques are two commonly used methodologies.

Two-dimensional  $^{31}\text{P}$  and  $^1\text{H}$ -NMR exchange methods complement these techniques and provide some subtle advantages. Using examples drawn from simple coordination chemistry of Pt(II), followed by some rather complicated simultaneous exchange phenomena involving  $\text{Pt}\{\text{CH}_2\text{C}(\text{CH}_3)\text{CH}_2\}(\text{SnCl}_3)(\text{styrene})$  we will demonstrate the strength and weakness of this methodology.

In a second chapter we will illustrate some few applications of inverse 2-D X nucleus-NMR spectroscopy where subtle structural questions were solved using metal atom NMR data.

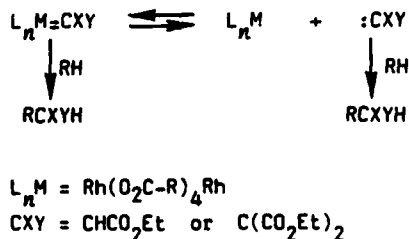
### III. RHODIUM(II) CARBOXYLATE-CATALYSED REACTIONS OF DIAZOESTERS : AN EQUILIBRIUM BETWEEN FREE CARBENE AND A METAL-CARBENE COMPLEX

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A comparative study of alkane homologation by ethyl diazoacetate and diethyl diazomalonate, catalysed by various rhodium(II) carboxylates, indicates that two different active carbene species, a metal-carbene intermediate and presumably the "free" carbene, are involved in these reactions.

Indeed, we have observed that the homologation of alkanes by ethyl diazoacetate dramatically depends on the method of decomposition (photolysis, thermolysis, or catalysis) of the diazo compound and on the nature of the rhodium(II) counter-ions. This is consistent with the involvement of the previously proposed metal-carbene intermediate\*.

On the contrary, several characteristics of the functionalisation of alkanes by diethyl diazomalonate are almost independent on the mode of decomposition of the diazo precursor, as well as on the ligands of the rhodium catalyst. This suggests a different active species that does not include the metal. Therefore, the free carbene formed by dissociation of the metal-carbene complex is a good candidate within the possible following mechanism :



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A. Demonceau, A.F. Noels, J.-L. Costa, and A.J. Hubert, submitted for publication.

THE REACTION OF A RUTHENIUM(II) DICHLOROCARBENE COMPLEX WITH PYRROLE:  
THE DIPYRRROMETHYLIDENE LIGAND.

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Metal bound electrophilic dihalocarbene centres can, in an intra-molecular reaction, add to the phenyl rings of *cis*-coordinated  $\text{PPh}_3$  ligands<sup>1</sup>. In a related intermolecular version of this reaction, the electrophilic carbene centre in  $\text{RuCl}_2(=\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$ <sup>2</sup> has been found to add to the aromatic heterocycle, pyrrole, to form  $\text{RuCl}_2[\text{C}(\text{Cl})(2\text{-C}_4\text{H}_4\text{N})](\text{CO})(\text{PPh}_3)_2$  (1). The structure of this complex has been determined by X-ray crystallography and noteworthy features are the long  $\text{C}_{\text{carbene}}\text{-Cl}$  bond, the large  $\text{Ru-C}_{\text{carbene}}\text{-C}_{\text{pyrrole}}$  angle and the hydrogen bonding of the N-H proton to the *cis* metal bound chloro-ligand.

Compound (1) undergoes further reaction with pyrrole, in the presence of base, forming  $\text{RuCl}[\text{C}(2\text{-C}_4\text{H}_3\text{N})(2\text{-C}_4\text{H}_4\text{N})](\text{CO})(\text{PPh}_3)_2$  (2). Compound (2) adds HCl giving  $\text{RuCl}_2[\text{C}(2\text{-C}_4\text{H}_4\text{N})_2](\text{CO})(\text{PPh}_3)_2$  (3), while base reconverts (3) to (2). Compound (3) contains the novel dipyrromethylidene ligand and compound (2) has an unusual chelate ligand with both carbene and amido donor functions. The X-ray crystal structure of compound (2) and further reactions of compounds (1) - (3) will be reported.

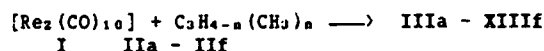
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**PHOTOCHEMICAL REACTIONS OF DECACARBONYLDIRHENIUM WITH ALLENE  
AND DERIVATIVES OF ALLENE**

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Decacarbonyldirhenium (I) reacts at low temperatures photochemically with mono-olefins, dienes or trienes predominantly under loss of CO and oxidative addition of a C-H-bond to octacarbonyl- $\mu$ -hydrido- $\mu$ - $\eta^{1:2}$ -olefinyl-dirhenium complexes <sup>1</sup>. With cumulated dienes like allene (IIa), and its methylated derivatives (IIb - IIi),  $[\text{Re}_2(\text{CO})_{10}]$  shows a totally different photoreactivity. A wide variety of mono- and dinuclear rhenium complexes are obtained, with allene, and hydrocarbon ligands, formed from the allenes by H-shift, dimerization and co-oligomerization with CO.



1,2-propadiene	(IIa)	IIIa, IVa, Va, VIa
1,2-butadiene	(IIb)	IIb, IVb
2,3-pentadiene	(IIc)	IIIc, IVc, VIIc, VIIIc
3-methyl-1,2-butadiene	(IIId)	IIId, VIId, IXd, Xd, XIId
2-methyl-2,3-pentadiene	(IIe)	IIIe, VIIe, VIIIe, IXe, Xe, XIIe
2,4-dimethyl-2,3-pentadiene	(IIi)	IXf, Xf, XIIIf

The types of products depend on the number and position of the methyl substituents in the allenes. Eleven different types of complexes were isolated by HPL chromatography. With the exception of IIi all allenes form  $[\text{Re}_2(\text{CO})_8(\mu-\eta^{2:2}-\text{C}_3\text{H}_{4-n}(\text{CH}_3)_n)]$  (IIIa - IIIi;  $n = 0 - 3$ ) with bridging allene ligands. With IIa - IIc  $[\text{Re}_2(\text{CO})_9(\mu-\eta^{2:1}-\text{C}_3\text{H}_{4-n}(\text{CH}_3)_n)]$  (IVa - IVc;  $n = 0, 1, 2$ ) are the common products. Allenes with two and three methyl groups add hydrogen and form the simple enyl complexes  $[\text{Re}(\text{CO})_4(\eta^3-\text{C}_3\text{H}_5-n(\text{CH}_3)_n)]$  (VIIc - VIIi;  $n = 2, 3$ ). In addition, IIId - IIi show a metal induced isomerization to the corresponding conjugated dienes in  $[\text{Re}_2(\text{CO})_8(\mu-\eta^{2:2}-\text{C}_4\text{H}_6-n(\text{CH}_3)_n)]$  (IXd - IXi;  $n = 1, 2, 3$ ), and  $[\text{Re}_2(\text{CO})_9(\mu-\text{H})(\mu-\eta^{1:2}-\text{C}_4\text{H}_5-n(\text{CH}_3)_n)]$  (Xd - Xi;  $n = 1, 2, 3$ ).

Unique products are obtained in several cases. 2-Methyl-2,3-pentadiene (IIe) forms by 1,2-H-shift a trimethylated bridging propenyliden ligand, found in the carbene complex  $[\text{Re}_2(\text{CO})_8(\mu-\eta^{1:2}-\text{CH}_2\text{CCH}(\text{CH}_3)_2)]$  (XIIe). Only 3-methyl-1,2-butadiene (IIId) shows a co-oligomerization with CO to 2,5-di-*i*-propenylcyclopentanone. The cyclopentanone is coordinated in its enol form as a 4-electron donor by a CC-double bond and the oxygen to the  $(\text{CO})_5\text{Re}_2(\text{CO})_3$  fragment in XIId. The permethylated allene IIi forms tricarbonyl- $\eta^3$ -2,4-dimethyl-2,4-pentadien-1-yl-rhenium (XIIIi).

Three types of complexes with allene dimers as ligands were isolated. Allene (IIa) yields a  $[\text{Re}_2(\text{CO})_8]$  complex with tetramethylenethane (Va) and a  $[\text{Re}_2(\text{CO})_7]$  complex with vinyltrimethylenemethane (VIa) as bridging ligands. IIc and IIe form  $[\text{Re}_2(\text{CO})_7]$  complexes with  $\eta^{1:2:1:2}$ -1,5-hexadien-2,5-diyl and CO bridges.

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Water Oxidative Addition to Pd(0) Phosphine Complexes in the Presence of Lewis Bases.

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Hydrido-hydroxy complexes derived from water oxidative addition to transition metals are supposed to be intermediates in water activation. Late-transition metal complexes tend to form unstable metal hydrido-hydroxy derivatives (e.g.  $\text{Pt}(\text{H})(\text{OH})(\text{PR}_3)_2$ )<sup>1</sup>, and only recently a full characterization of a stable hydrido-hydroxy iridium complex has been reported<sup>2</sup>. We report here the preparation and characterization of a Pd(II) phosphine complex derived from oxidative addition of water in the presence of Lewis acids.

$\text{Pd}(\text{PCy}_3)_2$  (Cy = cyclohexyl) reacts in toluene solution with water in the presence of a stoichiometric amount of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  yielding the colourless insoluble complex  $[\text{Pd}(\text{H})(\text{OH})(\text{PCy}_3)_2] \cdot \text{BF}_3$ . This compound, which can be handled at room temperature for some hours both in the solid state and in solution without noticeable decomposition, has been fully characterized by analytical and spectroscopic data.

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<sup>57</sup>Fe MOSSBAUER AND <sup>31</sup>P NMR SPECTROSCOPIC CHARACTERIZATION OF  
Fe(CO)<sub>3</sub>L'L' COMPLEXES (L', L' = PHOSPHITE OR PHOSPHINE)

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A variety of mixed ligand complexes of the type Fe(CO)<sub>3</sub>L'L' (L' = triphenylphosphine or triphenylphosphite and L' = phosphine or phosphite) have been synthesized by the stepwise reactions of phosphine and phosphite with iron dodecacarbonyl. These mixed ligand complexes provide a good opportunity to study the Fe-P bond by <sup>57</sup>Fe Mössbauer and <sup>31</sup>P NMR spectroscopy. All the <sup>57</sup>Fe Mössbauer spectra of trans-Fe(CO)<sub>3</sub>L'L' gave a quadrupole-splitting doublet typical of the disubstituted iron carbonyls in trigonal bipyramidal symmetry. The isomer shift and the quadrupole splitting fall into the range characteristic of disubstituted iron carbonyls with D<sub>3h</sub> symmetry. A linear correlation with a positive slope was found between the quadrupole splittings and the isomer shifts. This linear correlation indicates that the iron-to-phosphorus σ-donation is offset by the phosphorus-to-iron π-back donation. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of trans-Fe(CO)<sub>3</sub>L'L' complexes gave a couple of doublets assignable to the coordinated phosphite and/or the coordinated phosphine. As expected, the doublet of the phosphite-coordinated site was observed at the downfield compared with that of the phosphine-coordinated site. The change in the chemical shift upon coordination of the phosphine and phosphite ligand, i.e. the coordination shift is associated with the Mössbauer isomer shifts. This suggests that the iron-to-phosphorus π-back donation plays an important role in the formation of the Fe-P bond. A larger coupling constant of <sup>3</sup>J(P,P) was observed for trans-Fe(CO)<sub>3</sub>L'L' (L' = triphenylphosphite and L' = phosphines), while a smaller coupling constant was found for trans-Fe(CO)<sub>3</sub>L'L' (both L' and L' = phosphines or phosphites). The relatively large coupling constant due to <sup>3</sup>J(P,P) means that there exists a strong interaction between trans phosphorus ligands through the P-Fe-P bond. The <sup>3</sup>J(P,P) coupling constant reflects the bond strength between Fe-P and the Mössbauer isomer shift is also a measure of the strength of the Fe-P bond. In view of this feature a correlation between these spectroscopic parameters will be discussed for trans-Fe(CO)<sub>3</sub>L'L' complexes.

**Organometallic Chemistry of Chelating Oxygen Ligands:  
Coordination and Catalysis.**

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We have recently reported that anionic complexes of the type  $L^- = [CpM(P(O)R_2)_2]^-$  ( $Cp = C_5H_5$ ,  $C_5Me_5$ ,  $M = Co, Rh$ ) react as tris-chelating oxygen ligands with a large variety of metal ions to form stable 2:1 and 1:1 complexes, e.g.  $[ML_2]^{(2-2)+}$ ,  $M^{2+} = Ti - Zn$ ,  $LZrCl_2$ ,  $LMo(O)Cl_2$ ,  $L_2W_2O_5$ , and  $[LRhCl_2]^-$ .<sup>1,2</sup> The ligand field spectra of the transition metal complexes  $[ML_2]$  (where the metal ion  $M$  is octahedrally coordinated by six  $P=O$  oxygen donor centers) allow an unequivocal determination of the electronic properties of the ligands  $L^-$ : they are very weak and hard oxygen ligands, comparable to fluoride and oxide in their ligand field strength and about as hard as water.<sup>1</sup> We were therefore surprised to see that most of the organometallic complexes<sup>3</sup> containing oxygen tripod ligands of the type  $L^-$ , e.g. the molybdenum and tungsten compounds  $LM(CO)_3H$ ,  $LM(CO)_2(\eta^2-C(O)R)$ ,  $LM(=CPh)(CO)_2$ ,  $L_2M_2(CO)_4$  ( $M=M$ ), and others like  $L(Mn(CO)_3)$ ,  $LRu(CO)_2Cl$ ,  $L_2Ru_2(CO)_4$  ( $Ru-Ru$ ),  $LRh(\mu-CO)_3RhL$  ( $Rh-Rh$ ),  $LRh(C_2H_4)_2$ ,  $LCu(CO)$ ,  $LCu(PhC=CPh)$  are very stable.

In order to prepare more reactive organometallic derivatives two routes have been envisaged: functionalization of the ligands  $L^-$  with the aim of introducing additional labile coordination sites or the substitution of a labile chloride donor site for one of the strongly coordinating  $P=O$  oxygen donor centers. An example for the latter possibility is the anionic complex  $[(C_5Me_5)RuCl(P(O)R_2)_2]^-$ ,  $R = OCH_3$ , which has been shown to act as a ligand with an  $O,O,Cl$  donor set.<sup>4</sup>

Several of the chelating oxygen ligands have successfully been used as components in catalysts for the cyclotrimerisation of acetylenes and hydroformylation or hydrogenation of olefins.

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REDOX CHEMISTRY OF DIPHOSPHAZANE LIGAND BRIDGED DERIVATIVES OF  
DIRUTHENIUM NONACARBONYL

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Reaction of  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2]$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^i$ ), electron-rich derivatives of  $[\text{Ru}_2(\text{CO})_8]$  with compounds or salts of  $\text{Cu(I)}$ ,  $\text{Au(I)}$  or  $\text{Hg(II)}$  gives cationic products in which the Group IB or Group IIB metal substrate is co-ordinated either terminally as in  $[\text{Ru}_2(\text{HgCl})(\text{CO})_5\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2]^+$ , or in the bridging mode as in  $[\text{Ru}_2\{\mu\text{-Au(PPh)}_3\}\{\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2\}_2]^+$ , the structure of the latter being established X-ray crystallographically. Treatment of  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]$  (1) with  $\text{Ag(I)}$  salts leads to products whose nature depends on the ligand co-ordinated to the silver. For instance, reaction of (1) with an equimolar amount of  $\text{AgSbF}_6$  in weakly co-ordinating oxygen-donor solvents such as acetone or THF leads to the formation of a half-molar amount of  $[\text{Ru}_2(\text{CO})_5(\text{solvent})\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]^+$  (2) and the precipitation of elemental silver. On the other hand reaction of (1) with  $\text{AgSbF}_6$  in MeCN or with  $[\text{Ag}(\text{pyridine})_4]\text{SbF}_6$  in THF, gives  $[\text{Ru}_2\{\mu\text{-Ag(L)}\}\{\mu\text{-CO})(\text{CO})_4\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]^+$  ( $\text{L} = \text{MeCN}$  or  $\text{C}_5\text{H}_5\text{N}$ ). Solid  $[\text{Ru}_2\{\mu\text{-Ag(MeCN)}\}\{\mu\text{-CO})(\text{CO})_4\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2][\text{SbF}_6]$  degrades under vacuum to the one-electron oxidised product  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2][\text{SbF}_6]$  (3,  $\text{SbF}_6$ ), elemental silver and acetonitrile; (3) rapidly disproportionates in solution to give (1) and (2) an observation which is confirmed by cyclic voltammetric studies of the electrochemical oxidation of (1) in acetone and benzonitrile. Thus the one-electron oxidation of (1) by certain silver salts to give (3) is shown to proceed via an inner-sphere mechanism. The usefulness of the dicationic solvento species (2) as a precursor for the synthesis of diruthenium compounds is demonstrated by its facile reaction with neutral e.g.  $\text{L} = \text{CO}$  and  $\text{RNC}$ , and anionic e.g.  $\text{X}^- = \text{H}^-$ ,  $\text{CN}^-$ ,  $\text{OMe}^-$  and  $\text{MeCO}_2^-$ , nucleophiles to give  $[\text{Ru}_2(\text{CO})_5\text{L}\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]^+$  and  $[\text{Ru}_2(\text{CO})_5\text{L}\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]^+$  and/or  $[\text{Ru}_2(\mu\text{-X})(\text{CO})_4\{\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2\}_2]^+$ .

A DOMINANT ROLE FOR STERIC EFFECTS IN THE CHEMISTRY OF  
RUTHENIUM(II) COMPLEXES WITH 1,2-BIS(DICYCLOHEXYLPHOSPHINO)ETHANE

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Ruthenium(II) forms six-coordinate complexes of the type  $RuX_2(P-P)_2$  ( $X$ =halogenide) with some diphosphine ligands [ $P-P = R_2P-(CH_2)_n-PR_2$ ;  $n = 1, 2, 3$ ;  $R = Me, Et, Ph$ ].<sup>1</sup> However, with the ligands which form six-membered chelate rings ( $n=3$ ,  $R=Ph$ ), also the five-coordinate cations  $[RuX(P-P)_2]^+$  have been obtained. We now find that analogous five-coordinate complexes can be prepared also with ligands forming five-membered chelate rings, if the  $R$  substituents at the phosphorus atoms are the bulky cyclohexyl groups. The five-coordinate complexes  $[RuX(dcpy)_2]BPh_4$  [ $dcpy = 1,2$ -bis(dicyclohexylphosphino)ethane;  $X = Cl, Br, I$ ], formed by reacting  $dcpy$  with  $RuX_2(DMSO)_4$  and an excess of  $NaBPh_4$  in ethanol, are fluxional at room temperature on the NMR time scale, and show at low temperature a spectral pattern which suggests a trigonal-bipyramidal structure.

Since there is evidence from both theoretical studies and solid state analyses that five-coordinate  $d^6$  complexes prefer the square-pyramidal geometry over the isomeric trigonal-bipyramidal form, the molecular structure of  $[RuCl(dcpy)_2]PF_6$  has been determined by X-ray diffractometry. The complex is based on the TBP geometry with two  $P$  atoms at the axial positions and two  $P$  atoms and the chloride in the equatorial plane. Distortions from the idealized geometry can be attributed both to the bite of the diphosphine ligands and to the steric requirements of the cyclohexyl groups.

According to their coordinatively unsaturated nature, the complexes  $[RuX(dcpy)_2]^+$  readily add carbon monoxide to yield  $trans-[RuX(CO)(dcpy)_2]^+$ , and their dissolution in a coordinating solvent such as acetonitrile occurs with the formation of the six-coordinate adducts  $trans-[RuX(CH_3CN)(dcpy)_2]^+$ . Consistently with the  $trans$ -structure, the  $^{31}P$  NMR spectra of both carbonyl and acetonitrile six-coordinate derivatives show a single sharp signal at room temperature. However, when the temperature is lowered, the singlet broadens, and at 143 K gives rise to a complex pattern which is consistent with an  $AA'BC$  spin system. These NMR results have been explained in terms of the steric crowding of the cyclohexyl groups which interact in such a way to destroy the symmetry of the six-coordinate molecule, with the ligand motions sufficiently restricted that the reduction of symmetry is maintained in the NMR time scale.

These results show that the chemistry of both six- and five-coordinate derivatives of ruthenium(II) with  $dcpy$  is largely determined by the bulkiness of the diphosphine ligand.

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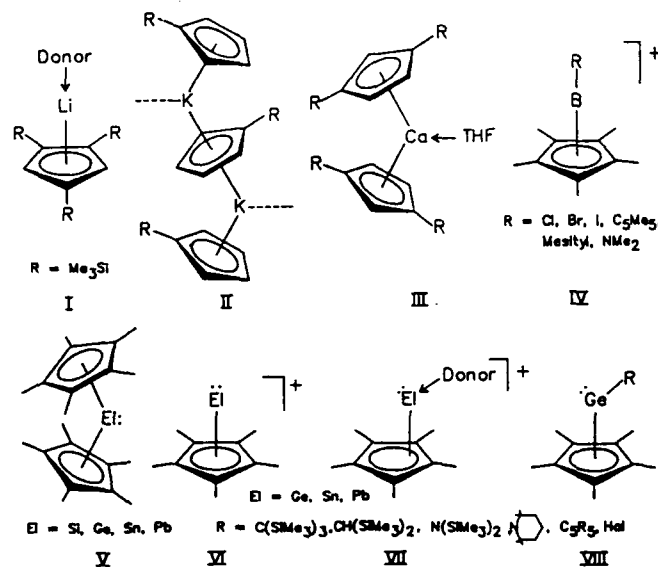
## MAIN GROUP METALLOCENES - RECENT DEVELOPMENTS

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$\pi$ -Complexation has become an interesting tool in main-group chemistry, as documented by many mainly recent examples [1,2]. The central atoms in the resulting compounds are characterized by low oxidation states and high coordination numbers. Here, some new results concerning synthesis, structure, bonding, and reactivity of  $\pi$ -cyclopentadienyl species are reported.

With trimethylsilylated cyclopentadienyl ligands, hitherto unknown structures are verified in group 1 and group 2 chemistry (see I, II and III).

The pentamethylcyclopentadienyl ligand stabilizes cationic species of type IV in boron chemistry; in group 14,  $\pi$ -complexes of type V - VIII have been realized.



Special emphasis will be given to the synthesis and structure of decamethylsilicocene, (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Si, the first silicon(II) compound stable under ordinary conditions. The chemistry of this  $\pi$ -complex differs importantly from that of the heavier homologues.

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**SYNTHESIS, CHARACTERIZATION AND ANTITUMOUR ACTIVITY OF  
"PARATIN", AN ORGANOTIN(IV) ANALOG OF "PARAPLATIN"  
("CARBOPLATIN"), AND OF SOME RELATED COMPOUNDS**

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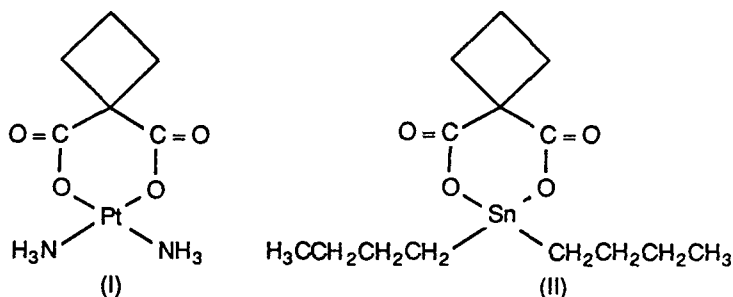
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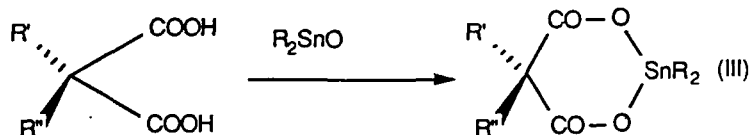
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The antitumor activity of "paraplatin", (I) was found superior to that of "cis-platin", cis-Cl<sub>2</sub>Pt(NH<sub>3</sub>)<sub>2</sub>, in two xenograft systems, colon CX-1 xenograft and epidermoid carcinoma P-246 xenograft, and also against PC 6A plasmacytoma<sup>(1)</sup>.



Because many diorganotin compounds exhibit some antitumor activity<sup>(2)</sup>, we have prepared in high yield "paratin", (II), an analog of paraplatin, and also some other related di-n-butyltin(IV) derivatives, (III).



Their spectroscopic properties (<sup>1</sup>H, <sup>13</sup>C NMR, Mössbauer, IR, and mass spectrometry), used to characterize them, will be discussed, together with the results of the *in vitro* and *in vivo* screening.

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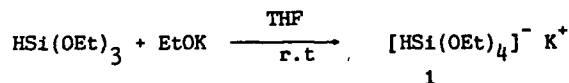
PENTACOORDINATE SILICON SPECIES : SYNTHESIS AND REACTIVITY  
OF NOVEL HYDRIDOALKOXOSILICATES

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Pentacoordinate hydridosilicates have been assumed as active hydride species of reduction of carbonyl compounds with hydridosilanes promoted by fluoride or alkoxide ions.

We have now prepared several pentavalent hydridoalkoxosilicate anions for the first time. For instance, reaction of potassium alkoxide with triethoxysilane yielded quantitatively the potassium salt of the hydridotriethoxosilicate, 1, as a white powder :



We examined their chemical behaviors :

- Reactions of 1 with aldehydes and ketones proceed smoothly in THF at 0°C or r.t. to afford the alcohol in high yields after hydrolysis.
- Nucleophilic displacement reactions (Nu = RMgX, ROH, H<sub>2</sub>O) can be performed.
- Interestingly, reduction is observed in the reactions of 1 with alkyl halides.

The above data will be discussed and compared to those obtained with the corresponding neutral tetravalent species.

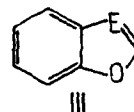
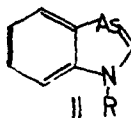
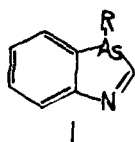
THE CONJUGATIVE ABILITY OF PHOSPHOROUS AND ARSENIC,  
A UPS STUDY

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The conjugative ability of phosphorous and arsenic is generally thought to be similar to that of nitrogen. In the latter case conjugation with a  $\pi$  system can be attained by two different ways. One of them is that nitrogen takes part in double  $\pi$  bonds as the case is in imines, piridine etc., while the other possibility is the conjugation of the nitrogen lone pair with the  $\pi$  system as in aniline, pyrrole etc.

Our photoelectron spectroscopic investigations on aniline analogues showed small interaction between the  $\pi$  system and the phosphorous or arsenic lone pair. Similar conclusion could be drawn by investigating the 3-substituted 1,3-benzazaarsole (I) system.



The 1-substituted 1,3-benzazaarsole system (II), however, shows a large conjugation of the arsenic-carbon double bond and the  $\pi$  system, similarly to the compounds of type III.

The authors thank for the financial support of National Scientific Research Foundation of Hungary (Nr. 487/86).



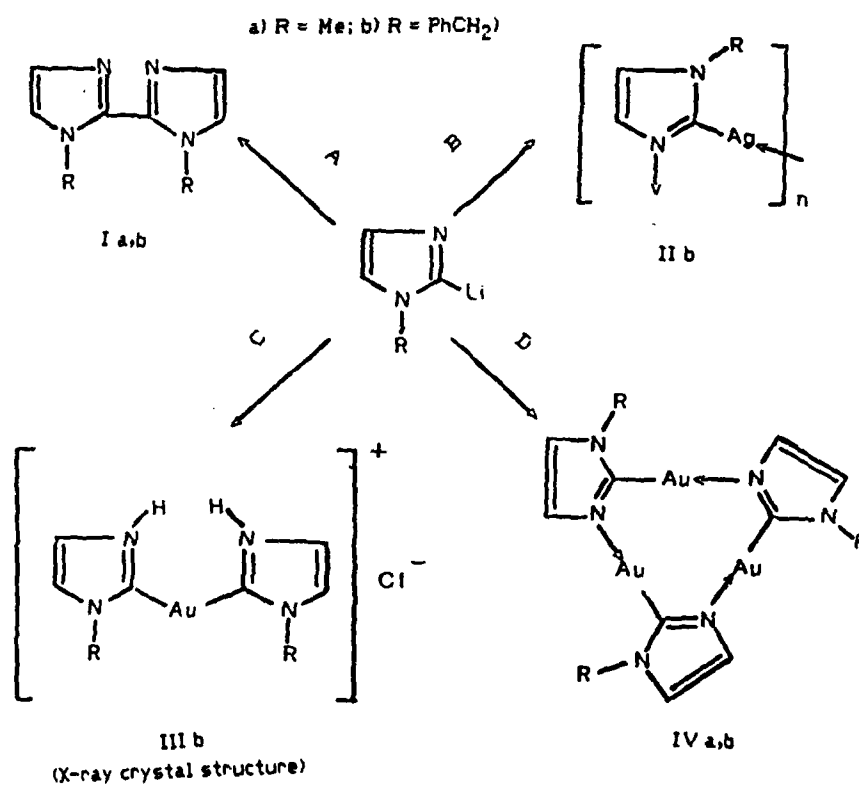
## GOLD AND SILVER IMIDAZOLE DERIVATIVES HAVING METAL-CARBON BOND(S).

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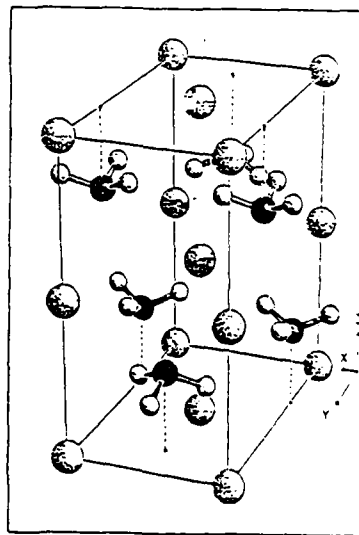
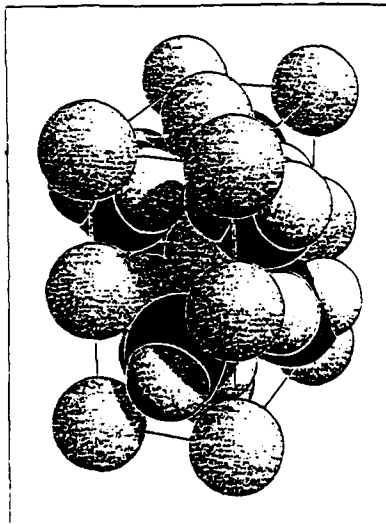
A) Me<sub>2</sub>SCuBr (R = Me or PhCH<sub>2</sub>)B) Me<sub>2</sub>SAgNO<sub>3</sub> (R = PhCH<sub>2</sub>)C) t-Bu<sub>3</sub>PAuCl (R = PhCH<sub>2</sub>)D) Ph<sub>3</sub>PAuCl or Me<sub>2</sub>SAuCl (R = Me or PhCH<sub>2</sub>)

**STRUCTURE REFINEMENT OF METHYL POTASSIUM  
PREPARATION OF  $\text{KCH}_3\text{-d}_3$  AND NEUTRON DIFFRACTION STUDY  
AT 1.35 AND 290 K**

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The crystal structure of methyl potassium has been refined by neutron diffraction at 1.35 and 290 K using powder samples of  $\text{KCD}_3$ . Slightly distorted pyramidal methyl ions of  $C_3$  symmetry were found with bond angles analogous to  $\text{NH}_3$ . In the crystal each carbanion is coordinated by six K ions with a trigonal-prismatic array and the methyl ions have alternating orientations. An orthorhombic unit cell ( $\text{Pmcn}$ ,  $a=419.80(5)$ ,  $b=727.98(8)$ ,  $c=215.22(8)$  pm,  $Z=4$ ) has now been found as compared to the smaller hexagonal cell ( $Z=2$ ) detected previously [1] by X-ray methods and without precise location of the H atoms. The preparation of  $\text{KCD}_3$  and  $\text{LiCD}_3$  is described together with IR data of  $\text{KCD}_3$ .



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## On the Structure and Bonding in Cyclopentadienyl Compounds of In(I) and Tl(I).

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In the solid state both  $\text{In}(\text{C}_5\text{H}_5)$  and  $\text{Tl}(\text{C}_5\text{H}_5)$  exhibit polymeric zig-zag chain structures, where the metal atoms are pentahapto bonded to two bridging cyclopentadienyl rings with linear metal-ring centroid-metal fragments and ring centroid-metal-ring centroid angles of approximately  $137^\circ$ .<sup>1</sup> The introduction of bulky groups on the cyclopentadienyl rings increase the steric repulsions between the chains, which in the case of  $\text{In}(\text{C}_5\text{Me}_5)$  leads to a solid state structure where six Indium atoms form an octahedral cluster with each pentamethylcyclopentadienyl ring pentahapto bonded to only one Indium atom,  $[\text{In}(\text{C}_5\text{Me}_5)]_6$ .<sup>2</sup> In the three cyclopentadienyl indium structures that have been reported, the direct In-In distances are all in the range 394-399 pm, indicating that these interactions are the determining factors for how the total structures turn out. The structural consequences when sterically bulky groups are introduced on the ring are less for the Thallium analogue;  $\text{Tl}(\text{C}_5\text{Me}_5)$  can still maintain the zig-zag chain structure.<sup>3</sup> The structural differences between the indium and thallium analogues in the solid state seem to be a consequence of decreased metal-metal bonding capability when going down group 13. In the cyclopentadienyl-thallium compounds the  $\text{Tl}\cdots\text{Tl}$  interactions are weaker, so when the substituents on the cyclopentadienyl ring are bulkier the zig-zag structures can still be maintained by loosening up the interchain  $\text{Tl}\cdots\text{Tl}$  interactions.

In the gas phase both  $\text{In}(\text{C}_5\text{H}_5)$  and  $\text{Tl}(\text{C}_5\text{H}_5)$  form monomeric units with open-faced half sandwich structures of  $\text{C}_{5v}$  symmetry.<sup>4</sup> The gas phase structure of  $\text{In}(\text{C}_5\text{Me}_5)$  is similar to the non methylated compound; the only difference being a shortening of the In-C bond distance by approximately 3 pm;  $r(\text{In-C}) = 259.2(4)$  and  $261.9(5)$  pm in  $\text{In}(\text{C}_5\text{Me}_5)$  and  $\text{In}(\text{C}_5\text{H}_5)$  respectively. The same decrease of the metal-carbon bond distance has been observed for the thallium analogues. *Ab initio* calculations on  $\text{In}(\text{C}_5\text{H}_5)$  and  $\text{In}(\text{C}_5\text{Me}_5)$  indicate that the shortening of the metal-carbon bond is a consequence of the polarisation of negative charge on the ring towards the methyl groups.

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# NEW METHODS FOR GENERATING VOLATILE ORGANOMETALLIC SPECIES FOR ANALYSIS FROM THE ENVIRONMENT

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Numerous organometallic species are found in the natural environment<sup>1</sup>. Some of these arise from the use of various commercial products (e.g. agricultural chemicals, biocides, etc.) and some are formed in the environment (e.g. various methyl metal species). In the aqueous natural environment, these compounds are usually bound by naturally occurring proteinaceous ligands (via S, N or O atoms) in suspended or bottom sedimentary material. Analysis of these bound organometallics (e.g.  $\text{CH}_3\text{Hg}^+$ ,  $(\text{nC}_4\text{H}_9)_3\text{Sn}^+$ ,  $(\text{CH}_3)_2\text{AsOOH}$ , etc.) is made more difficult by their low concentrations and also by the need for extraction and removal of the organometallic from the environmental matrix prior to determination. In most cases, complete removal from the matrix for analysis does not occur; sometimes extraction is not only incomplete but it is also not very reproducible. A common procedure is to remove the non-volatile and relatively intractible organometallic from the environmental matrix by a derivatization technique that produces a volatile product retaining the organometallic features of the analyte (e.g. conversion of complexed  $(\text{nC}_4\text{H}_9)_3\text{Sn}$  to  $(\text{nC}_4\text{H}_9)_3\text{-SnH}$ ; conversion of  $(\text{CH}_3)_3\text{Ph}$  derivatives to  $(\text{CH}_3)_3\text{PhC}_2\text{H}_5$ ).

Several techniques are described in this paper for the extraction of various volatile hydride or ethyl derivatives of the following:  $\text{R}_3\text{Sn}^+$ ,  $\text{R}_2\text{Sn}^{2+}$ ,  $\text{RSn}^{3+}$ ,  $(\text{CH}_3)_2\text{As}^+$ ,  $\text{CH}_3\text{As}^{2+}$ ,  $(\text{CH}_3)_3\text{Pb}^+$ , inorganic tin, lead, antimony and arsenic compounds. Some techniques were applied to environmental aqueous solutions and some to complexes in sediment matrices. The techniques described involve a generation of the hydride or ethyl species on or off the column of a chromatograph and also include a convenient, one-step, non-Grignard process for generating ethyl derivatives for the analysis of organometallic derivatives from solution or sediments<sup>2-4</sup>. In the process for the extraction of organotin compounds from sediments, the analyte is extracted from acid solution by a tropolone/ $\text{CH}_2\text{Cl}_2$  solution. After concentration and re-solution in ethanol, ethyl derivatives were generated by addition of a  $\text{NaBEt}_4$  solution and the  $\text{R}_3\text{SnC}_2\text{H}_5$ /ethanol solution was analysed by GC AA or GC MS.

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BORON-CARBON  $\pi$ -BONDING IN THE FORMATION AND REACTIONS OF  
BORACYCLOPROPENES AND BORACYCLOPENTADIENES

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The question of the extent and chemical consequences of boron-carbon  $\pi$ -bonding in boracyclopolyenes has received considerable attention over the last 25 years [1]. However, only relatively recently have the unambiguous syntheses of the boracyclopropene (borirene) ring [2] and the boracyclopentadiene (borole) ring [3] been achieved.



In this report we describe our investigation of the di- $\pi$ -methane-like photorearrangement of diaryl(arylethynyl)boranes (III), which can lead to I or which in the presence of a diarylacetylene (IV) can effect the capture of a zwitterionic intermediate and thereby the generation of II. As an alternative approach to I, the photogeneration of carbene-like boron(I) intermediates and their capture by IV will be discussed.

The  $\pi$ -electron delocalization and the question of Hückel aromaticity in the borirene and borole systems will be assessed on the basis of the following criteria: 1) spectral properties of I and II, as well as their complexes with Lewis bases; 2) X-ray crystallographic data on B-C and C-C bond distances; 3) chemical reactivity of the boron-carbon rings; and 4) suggestive results of Extended Hückel Molecular Orbital calculations [4].

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# MIGRATORY INSERTION OF CARBON MONOXIDE INTO METAL ACYL BONDS TO FORM $\alpha$ -KETOACYL LIGANDS

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Oxidation of the anionic acyl complex  $[\text{Cp}'(\text{CO})_2\text{Mn-C(O)R}]^-$  ( $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_3$ ,  $\text{R} = \text{Ph}$ , Tol) followed by addition of NO gas yields the  $\alpha$ -ketoacyl complex  $\text{Cp}'(\text{CO})(\text{NO})\text{Mn-C(O)C(O)R}$ , for which the  $\text{R} = \text{Ph}$  derivative has been crystallographically characterized. This reaction sequence represents the first observed CO insertion into a metal-acyl bond and indicates that such reaction may be important in some of the metal catalyzed "double carbonylation" reactions. Similar treatment of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe-C(O)CH}_3$  with an oxidizing agent followed by NO addition gives the cationic  $\alpha$ -ketoacyl complex  $[\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe-C(O)C(O)CH}_3]^+$ . The intermediate  $17e^-$  complex resulting from the oxidation process has been spectroscopically detected in both the Fe and Mn reactions. A mechanism for this carbonylation is proposed which involves initial addition of NO to the oxidized complex as a *1e^-* donating bent nitrosyl ligand. This is believed to be followed by acyl migration to CO as the nitrosyl changes from a bent to a  $3e^-$  linear ligand, with the latter providing the driving force for the reaction.

A similar oxidation/NO addition reaction sequence has been found to convert the methyl complex  $\text{Cp}(\text{CO})(\text{PPh}_3)_2\text{Fe-CH}_3$  into the cationic acyl species  $[\text{Cp}(\text{NO})(\text{PPh}_3)\text{Fe-C(O)CH}_3]^+$ . This latter complex readily deprotonates to yield the unstable ketene complex  $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Fe(CH}_2\text{CO)}$  which rapidly disproportionates to form  $\text{Cp}_2\text{Fe}$  and  $\text{Fe}(\text{NO})_2(\text{PPh}_3)_2$ .

Oxidation has also been found to promote the carbonylation of carbene ligands to form ketenes, and these reactions will also be discussed.

The graduate students and postdoctoral fellows who have contributed to this research are Sherri Bassner, Sung-Hwan Han, and John Sheridan. This work has been supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

CHEMICAL FILIATIONS BETWEEN NEW HOMOBIMETALLIC  
COMPLEXES OF THE HETERODIFUNCTIONAL LIGAND  
(DIPHENYL PHOSPHINO) CYCLOPENTADIENYL

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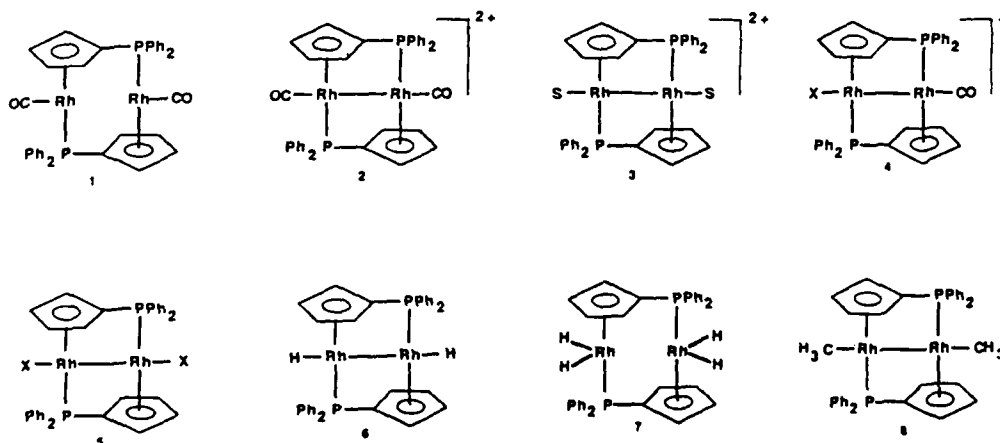
The homodimetallic complex 1 previously described (1) is easily chemically or electrochemically oxidizable according to a reversible two-electron process yielding the related symmetrical dication 2 which contains a metal-metal bond.

Complex 2 may be readily decarbonylated, using trimethylamine oxide, yielding complexes 3.

Treatment of 2 or 3 complexes with halides yields quantitatively mono or dihalide species such as 4 and 5.

Complex 5 is a convenient precursor to the preparation of dihydride 6, tetrahydride 7 and dimethyl 8 species.

Structural determinations (using NMR, IR, mass spectra and X-ray data) of these novel bimetallic species will be presented and discussed.



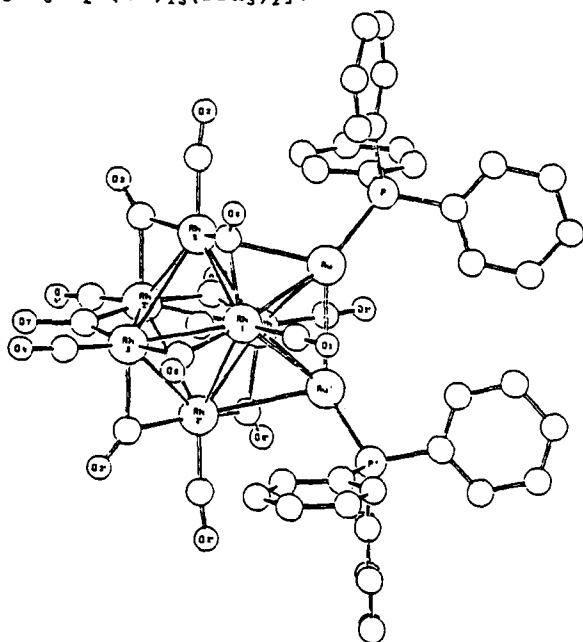
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BIMETALLIC CARBIDO CARBONYL CLUSTERS. SYNTHESIS AND STRUCTURAL  
CHARACTERIZATION OF  $[\text{Rh}_6\text{Au}_2\text{C}(\text{CO})_{13}(\text{PPh}_3)_2]$ .

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The prismatic carbido-carbonyl cluster  $[\text{Rh}_6\text{C}(\text{CO})_{15}]^{2-}$  undergoes electrophilic attack from metal fragments such as  $[\text{ML}]^+$  ( $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ), selectively on one or both triangular faces.<sup>2,3</sup> A parallel investigation on the octahedral anion  $[\text{Rh}_6\text{C}(\text{CO})_{13}]^{2-}$  gave, as result of the reaction with  $[\text{AuCl}(\text{PPh}_3)]$ , the new species  $[\text{Rh}_6\text{Au}_2\text{C}(\text{CO})_{13}(\text{PPh}_3)_2]$ .



Single crystal X-ray diffraction yielded the reported structure.<sup>5</sup> The molecule, with  $C_2$  symmetry, has a skeleton consisting of a distorted  $\text{Rh}_6$  octahedron capped on two adjacent faces by gold atoms which are bonded together with a distance of 2.929 Å. Other bond distances, in Å, are:  $\text{Rh1-Au}$ , 2.801;  $\text{Rh2-Au}$ , 3.147;  $\text{Rh1-Au}'$ , 2.859;  $\text{Rh1-Rh2}$ , 2.727;  $\text{Rh1-Rh3}$ , 2.795;  $\text{Rh1-Rh1}'$ , 3.245;  $\text{Rh3-Rh3}'$ , 2.808;  $\text{Rh1-Rh2}'$ , 3.230;  $\text{Rh2-Rh3}$ , 3.156;  $\text{Rh2'-Rh3}$ , 2.793. The interstitial carbide is located at an average distance of 2.063 Å from the rhodium atoms. The compound reacts with CO (1 atm, RT) to give the bicapped prismatic  $[\text{Rh}_6\text{C}(\text{CO})_{15}[\text{Au}(\text{PPh}_3)]_2]$ .<sup>3</sup>

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- 4) V.G. Albano, D. Braga and S. Martinengo, *J. Chem. Soc. Dalton Trans.*, 1981, 717.
- 5) Crystal data: orthorhombic, space group  $\text{Fdd2}$ ,  $a = 22.335(4)$ ,  $b = 31.710(6)$ ,  $c = 14.947(7)$  Å,  $Z = 8$ ,  $R = 0.04$ ,  $R_w = 0.05$ .



SYNTHESIS, CRYSTAL STRUCTURE AND SOLUTION CHEMISTRY  
OF THE TETRANUCLEAR ALKYNE COMPLEX

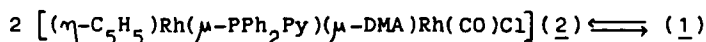


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The tetranuclear alkyne complex  $[(\eta-C_5H_5)Rh(\mu-PPh_2Py)-(\mu-DMA)Rh(CO)(\mu-Cl)]_2$  (1) ( $PPh_2Py$  = 2-(diphenylphosphino)pyridine) has been synthesized by reacting at room temperature the binuclear compound  $[(\eta-C_5H_5)Rh(\mu-CO)(\mu-PPh_2Py)Rh(CO)Cl]$  with the dimethyl acetylenedicarboxylate (DMA). The X-ray crystal structure of 1 was determined. The molecule shows a crystallographic inversion center originated from the presence of two asymmetrical bridging chloro-ligands which link two rhodium dimer units. Each dimer unit is completely asymmetrical and consists of two rhodium atoms bridged by the  $Ph_2PPy$  and the DMA which become bound as a dimetalated olefin.

Molecular weight determination showed that 1 is extensively dissociated at 298 K in  $CH_2Cl_2$ .  $^{31}P$  and  $^1H$  NMR data are consistent with the following temperature dependent equilibrium which takes place in solution:



The insaturation of the rhodium 16-electrons center seems to be a crucial point in the reactivity of 2. In fact it accounts for both the formation of the tetranuclear chloro-bridges dimers and for the reaction with small molecules such as  $SO_2$  and  $CO$ . In the latter case the  $CO$  addition product, formed in the first step, partially evolves at room temperature to new species. The  $^{13}C$  (212 ppm and 208 ppm) and the  $^1J(^{103}Rh-^{13}C)$  of 24 Hz are consistent with the formation of acyl derivatives, presumably by insertion of  $^{13}CO$  into a  $C-Rh$  bond. The  $CO$  reaction products have not been fully characterized owing to the reversibility of the process.

STRUCTURAL STUDIES OF PHOSPHINE SUBSTITUTED  $\text{HRuCo}_x\text{Rh}_{3-x}(\text{CO})_{12}$   
( $x = 0-3$ ) MIXED METAL CLUSTERS

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The trimetallic parent clusters  $\text{HRuCo}_2\text{Rh}(\text{CO})_{12}$  and  $\text{HRuCoRh}_2(\text{CO})_{12}$  were prepared as a mixture together with other tetra-nuclear clusters.<sup>1</sup>  $\text{HRuCo}_3(\text{CO})_{12}$  and  $\text{HRuRh}_3(\text{CO})_{12}$  were prepared separately according to known procedures. The tri-metallic clusters are difficult to isolate and they tend to decompose during the separation, but some of their phosphine derivatives can be isolated in small amounts by TLC on silica.

The crystal structures show  $\text{Rh}_4(\text{CO})_{12}$ -like carbonyl geometries (an example in Figure) with the hydride ligands bridging the basal metal face and phosphines being coordinated preferably on rhodium atoms in axial positions.

$^1\text{H}$  n.m.r. results, however, show that in solution the rhodium containing components have two isomers with the hydride bridging either a  $\text{Ru}(\text{apical})\text{-Rh}(\text{basal})$  edge or the basal face of the metal tetrahedron. Of these the face-bridged form, which in most cases dominates for the substituted compounds in solution, was found in the crystals. In solution the edge-bridging hydride tends to be connected with an equatorial phosphine.

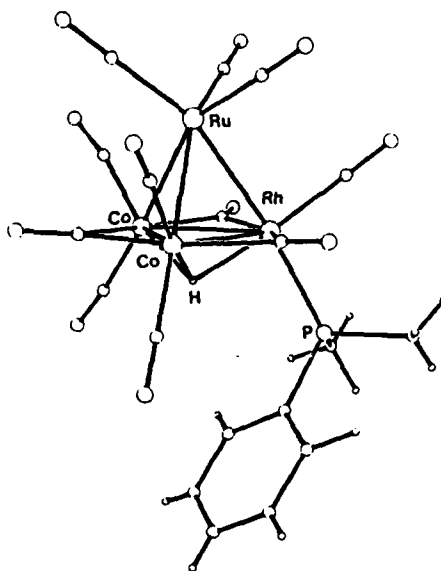


Figure.  $\text{HRuCo}_2\text{Rh}(\text{CO})_{11}(\text{PMe}_2\text{Ph})$

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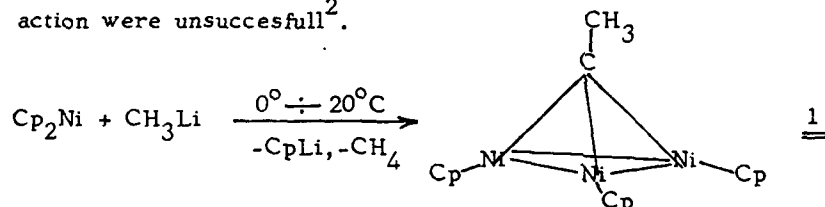
New tris/ $\eta^5$ -cyclopentadienylnickel/ $\mu_3$ -ethylidyne cluster

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Tris/ $\eta^5$ -cyclopentadienylnickel/ $\mu_3$ -alkylidyne clusters were obtained from the reaction of  $\text{Cp}_2\text{Ni}$  with benzylmagnesium chloride<sup>1</sup> or with alkyl-lithium  $\text{RCH}_2\text{Li}$  / $\text{R}=\text{CMe}_3$ ,  $\text{SiMe}_3$ /<sup>2</sup>. Both substrates don't contain  $\beta$ -H-atoms. The reaction of  $\text{Cp}_2\text{Ni}$  with  $\text{RCH}_2\text{M}$  / $\text{M}=\text{MgX}$ ,  $\text{Li}$ /, where organic substituent contains  $\beta$ -H atoms / $\text{R}=\text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}$ / leads to the decomposition of unstable  $\{\text{CpNiCH}_2\text{R}\}$  species /via  $\beta$ -H elimination/ and no  $\mu_3$ -alkylidynetrinickel / $\text{CpNi}/_3\text{CR}$  can be isolated<sup>3</sup>.

We observed that  $\text{Cp}_2\text{Ni}$  reacts with  $\text{CH}_3\text{Li}$  to give  $\mu_3$ -ethylidyne-trinickel cluster<sup>4</sup>, although previous attempts to isolate it from this reaction were unsuccessful<sup>2</sup>.



Besides 1, other clusters with more than three  $\text{CpNi}$  fragments are formed. 1 was isolated also from the reaction of  $\text{Cp}_2\text{Ni}$  with vinyl-lithium<sup>4</sup>. Full spectroscopic characterization of the cluster 1  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, MS, E.A as well as X-ray structure are given.

$\text{CpNiCp}^*/\text{Cp}^*=\text{C}_5\text{Me}_5/$  reacts with  $\text{CH}_3\text{Li}$  unselectively to give the mixture of  $[\text{Cp}_n\text{Cp}_{3-n}^*\text{Ni}]_3\text{CCH}_3$  clusters.

$[\text{Cp}^*\text{Ni}]_3\text{CCH}_3$  was isolated in the pure state after the sublimation off the mixed clusters followed by crystallization.

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**FERROCENYLSILYLMETHYLIDINETRICOBALTNONACARBONYL COMPLEXES.**

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Reaction between ferrocenyl silanes  $\text{FcSi(R)}_2\text{H}$  and  $1,1\text{-Fc}/[\text{Si(R)}_2\text{H}]_2$  [ $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$ ,  $1,1\text{-Fc}/ = (\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$ ,  $\text{R} = \text{Me, Et, Ph}$ ] and  $\text{HCCo}_3(\text{CO})_9$  leads to the preparation of the corresponding ferrocenylsilylmethylidinetricobaltnonacarbonyl complexes,  $\text{FcSi(R)}_2\text{CCo}_3(\text{CO})_9$  and  $1,1\text{-Fc}/\text{-}[\text{Si(R)}_2\text{CCo}_3(\text{CO})_9]_2$  in good yield. The  $^{29}\text{Si}$  nmr spectra of the complexes will be reported together with the crystal and molecular structure of the dicluster complex  $1,1\text{-Fc}/\text{-}[\text{Si(Me)}_2\text{CCo}_3(\text{CO})_9]_2$ .

Electrochemical studies of the mono- and dicluster complexes are consistent with electrochemically non-interacting ferrocene and cluster redox centres. A reversible one electron oxidation is centred on the ferrocenyl moiety with the  $\text{CCo}_3$  centres undergoing reversible one electron reduction.

Thermal and electron transfer catalysed substitution reactions with phosphine and phosphite ligands yield a variety of Lewis base derivatives of the cluster complexes. Chemical oxidation of the Lewis base derivatives yields both mono and dication products.

REACTIVITY OF  $[\text{HFe}_4(\text{CO})_{12}\text{BH}_2]$  ; A NOVEL CLUSTER WITH A BUTTERFLY METAL ARRANGEMENT.

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The novel cluster  $[\text{HFe}_4(\text{CO})_{12}\text{BH}_2]$  has been synthesised<sup>1,2</sup> and shown by X-ray analysis to adopt a butterfly metal framework.<sup>3</sup> Multideprotonation of the butterfly cluster  $[\text{HFe}_4(\text{CO})_{12}\text{BH}_2]$  has recently been achieved by the use of BuLi affording the anions,  $[\text{HFe}_4(\text{CO})_{12}\text{BH}]^-$ ,  $[\text{Fe}_4(\text{CO})_{12}\text{BH}]^{2-}$  and  $[\text{Fe}_4(\text{CO})_{12}\text{B}]^{3-}$  in high yields.<sup>4</sup> These anionic clusters have been characterised by i.r. and NMR spectroscopy (both  $^1\text{H}$  and  $^{11}\text{B}$ ). Reaction of these anionic clusters with the mononuclear cationic species containing labile acetonitrile ligands have been examined and the corresponding neutral clusters have been isolated and characterised by spectroscopic techniques. Complete detail regarding the synthesis, structure and NMR studies on these new clusters will be presented.

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### Carbonyl Scrambling in $\text{Fe}_3(\text{CO})_{12}$ , $\text{Ru}_3(\text{CO})_{12}$ , and their Derivatives.

by Brian E. Mann and Gary W. Bentley, Department of Chemistry,  
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An examination of the crystal structure of  $\text{Fe}_3(\text{CO})_{12}$  has revealed a new dynamic carbonyl scrambling mechanism involving concerted bridge opening and closing processes on different edges of the iron triangle. This is a very low energy pathway with  $\Delta G^\ddagger < 25 \text{ kJ mol}^{-1}$ . The  $^{13}\text{C}$  n.m.r. spectra of  $\text{Fe}_3(\text{CO})_{12-n}(\text{P}(\text{OMe})_3)_n$ ,  $n = 1$  to 3, in  $\text{CD}_2\text{Cl}_2$  at  $-100^\circ\text{C}$  are consistent with only this dynamic process occurring, but the merry-go-round process is just starting with  $\Delta G^\ddagger = 37$  to  $42 \text{ kJ mol}^{-1}$ . At  $-50^\circ\text{C}$ , an edge carbonyl scrambling process commences, and then at  $-30^\circ\text{C}$ , the trigonal twist comes into operation. The data unambiguously show that  $\text{Fe}_3(\text{CO})_{12-n}(\text{P}(\text{OMe})_3)_n$ ,  $n = 1$  or 2, and the major isomer of  $\text{Fe}_3(\text{CO})_9(\text{P}(\text{OMe})_3)_3$  exist in  $\text{CD}_2\text{Cl}_2$  solution in the carbonyl bridged form and have an activation energy of ca.  $40 \text{ kJ mol}^{-1}$  for merry-go-round carbonyl scrambling via the terminal carbonyl form. It is therefore probable that  $\text{Fe}_3(\text{CO})_{12}$  exists in  $\text{CD}_2\text{Cl}_2$  solution in exclusively the carbonyl bridged form found in the solid state.

A minor isomer of  $\text{Fe}_3(\text{CO})_9(\text{P}(\text{OMe})_3)_3$  exists without fully bridging carbonyls. This isomer is enhanced by increasing the bulk of the phosphite, and is dominant in  $\text{Fe}_3(\text{CO})_9(\text{P}(\text{OPr}^i)_3)_3$ . The  $^{13}\text{C}$  n.m.r. spectrum shows three carbonyl signals in the ratio 3:3:3. A structure analogous to that published for  $\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3$  is proposed with the axial carbonyls leaning into semi-bridging positions.

For  $\text{Ru}_3(\text{CO})_{12-n}(\text{P}(\text{OMe})_3)_n$ ,  $n = 1$  to 3, the lowest energy pathway is the merry-go-round process, with  $\Delta G^\ddagger < 30 \text{ kJ mol}^{-1}$ . The edge-bridging process is clearly observed in one isomer of  $\text{Ru}_3(\text{CO})_{10}(\text{P}(\text{OMe})_3)_2$ , with  $\Delta G^\ddagger = 37 \text{ kJ mol}^{-1}$ , and then at higher temperatures all the isomers show the trigonal twist mechanism.

CARBON-HYDROGEN BOND ACTIVATION AT DITUNGSTEN CENTERS SUPPORTED  
BY ALKOXIDE LIGANDS

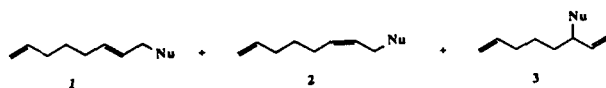
Malcolm H. Chisholm, Department of Chemistry, Indiana University,  
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Small alkoxide clusters of molybdenum and tungsten that are coordinatively unsaturated provide centers for the generation of organometallic chemistry by substrate binding and activation. Alternatively an organometallic chemistry can be brought about in a stepwise manner in which hydrocarbyl ligands are first introduced and then substrate binding and activation occurs. Examples of both approaches are described. (1) The reactions between  $W_2(OR)_4$  compounds ( $R = CH_2Bu^t$ ,  $Pr^i$ , cy-hexyl and cy-pentyl) and ethylene lead in a stepwise manner to (a) olefin adducts, (b) metallacyclopentanes and (c) alkylidyne ligands with the elimination of ethane. (2) The reactions between  $1,2-(RCH_2)_2W_2(OPr^i)_4$  compounds and alkynes ( $MeC\equiv CMe$ ,  $MeC\equiv CEt$  and  $EtC\equiv CEt$ ) yield alkyne adducts,  $W_2(CH_2R)_2(\eta^2-C_2R'_2)_2(OPr^i)_4$ ; alkylidyne-hydrides or -alkyls,  $W_2(\mu-C_4R'_4)(\mu-CR)(X)(OPr^i)_4$ , where  $X = H$  or  $CH_2R$ ; or alkyne adducts  $W_2(\mu-C_2R'_2)_2(OPr^i)_4$  or  $[(\eta^2-C_2R'_2)W_2(\mu-C_2R'_2)(\mu-CR)(OPr^i)_3]_2$  by competitive reaction pathways involving  $\alpha$  and  $\beta$  C-H activation. Mechanistic aspects of this reaction are discussed based on labelling studies.

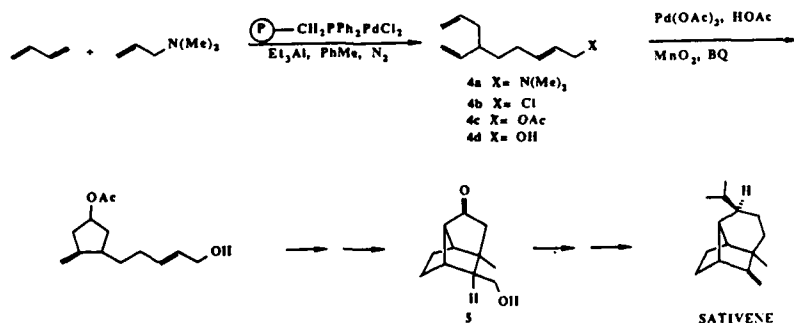
SELECTIVE PALLADIUM-CATALYZED TRANSFORMATIONS OF DIENES -  
FORMAL SYNTHESIS OF SATIVENE

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Products obtained by palladium-catalyzed telomerizations of conjugated dienes and nucleophiles have proved to be useful starting materials for a variety of natural products. However, in the telomerizations mixtures of octadienyl adducts 1-3 are usually obtained. We have found that using a catalyst prepared from  $\text{Pd}(\text{OAc})_2$ , a phosphine (or, preferably, a polymeric palladium-phosphine complex) and triethylaluminum in the reaction with diethylamine, the ratio 1:2:3 ( $\text{X}=\text{NET}_2$ ) varies with the  $\text{Pd:P:Al}$  ratio and under proper reaction conditions, the adduct 1 can be obtained without concomitant formation of 2 and 3.



These findings have been used in the synthesis of the Sativene precursor 5. The key steps are the regio- and stereoselective palladium-catalyzed telomerization of butadiene and  $\text{N,N}$ -dimethylallylamine to obtain 4a<sup>1</sup> and the regioselective palladium-catalyzed oxidative cyclization of 4d.<sup>2</sup>



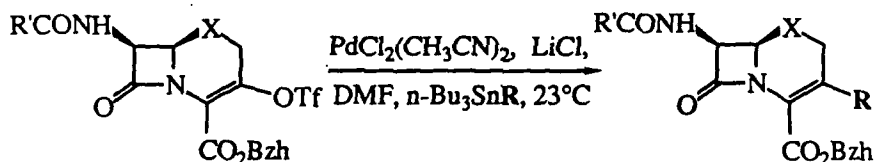
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Application of Palladium Catalyzed Organostannane Coupling  
with Vinyl Triflates to Complex  $\beta$ -Lactams

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We have developed methodology which allows palladium catalyzed couplings<sup>1</sup> to be applied to functionally complex  $\beta$ -lactam antibiotics. The coupling of 3-triflates of cepems and carbacepems with saturated and unsaturated organostannanes mediated by a palladium catalyst has been thoroughly explored. The (carba)cephem-3-triflates were highly catalyst selective unlike published examples and demanded the use of "ligandless" Pd(II) catalysts. This allowed the high yield application of this extremely chemoselective methodology to a large variety of organostannanes and  $\beta$ -lactam nuclei. Taking advantage of a side-reaction allowed the chemistry to be extended to novel palladium catalyzed reductions of enol triflates. Isolation and characterization of a presumed palladium containing intermediate is also described.



<sup>1</sup>See for example; W. J. Scott, G. T. Crisp, J. K. Stille, J. Am. Chem. Soc. 106 (1984) 4630.

ARENE SOLVATED COBALT ATOMS AS SOURCE OF NAKED CLUSTERS OF DIFFERENT SIZE AND SPECIFIC CATALYTIC ACTIVITY; PRELIMINARY EPR STUDIES.

Giovanni Vitulli, Sergio Bertozzi

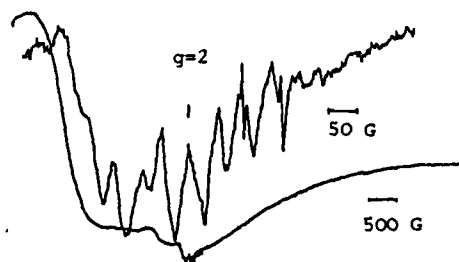
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Arturo Colligiani

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The clustering of solvated metal atoms is a promising tool for the preparation of naked clusters of different size and peculiar catalytic activity<sup>(1)</sup>. Arene solvated cobalt atoms, (arene=toluene, mesitylene), obtained by cocondensation of Co and arene vapours at about  $-196^{\circ}\text{C}$  followed by warming up to the melting temperature of the solvent, have recently been found to be very active catalysts in the synthesis of pyridines from acetylenes and nitriles<sup>(2)</sup>.

We report here epr evidence of the presence of cobalt clusters of different



size in such cocondensates. The epr spectrum recorded at about  $-35^{\circ}\text{C}$ , Figure 1, shows a group of structured signals, centred at  $g=2$ , which can be related to the presence of low-nuclearity Co clusters, and strong broad absorptions, accounting for high nuclearity Co aggregates<sup>(3)</sup>.

The clustering process is temperature dependent, allowing the separation of Co compounds of low and high nuclearity, showing different catalytic behaviours in the cocyclization of  $\alpha,\omega$ -dialkynes and nitriles to pyridines. Details on the magnetic properties of arene/cobalt cocondensates, at variable temperatures, will be given.

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ON THE SUBJECT OF IRON-GRAPHITE INTERCALATION COMPOUND AS A CATALYST FOR CONVERSION OF  $\text{CO} + \text{H}_2$  INTO ACETYLENE

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It was published recently that  $\text{FeCl}_3$  - graphite intercalation compound reduced by K-naphtalenide and further exposed to air was able to catalyse the unusual reaction of  $\text{CO} + \text{H}_2$  conversion into acetylene [1]. In this connection, we have examined a number of graphite intercalation compounds as Fisher-Tropsch catalysts.  $\text{FeCl}_3$  and  $\text{FeCl}_2$ -graphite intercalates of different stages (from 1 to 4) were reduced by alkali metals or by Li, Na and K-naphtalenides. These materials - per se or exposed to air prior to testing - were used as catalysts of  $\text{CO} + \text{H}_2$  reaction carried out under 100-300°C.

In all the cases products appeared to be the mixture of light hydrocarbons. Occasionally  $\text{C}_2\text{H}_2$  was indeed observed but in rather small quantity.

In the course of the investigation we found out that lithium reacted with naphtalene to give carbide-like compound which yielded  $\text{C}_2\text{H}_2$  after hydrolysis. The mild heating (70°-100°C) of this compound, exposed to air prior to the experiment, was followed by long-term process of  $\text{C}_2\text{H}_2$  evolution.

Therefore, the  $\text{C}_2\text{H}_2$  formation in [1] seems at least partly to be the result of the naphtalene with alkali metal reaction.

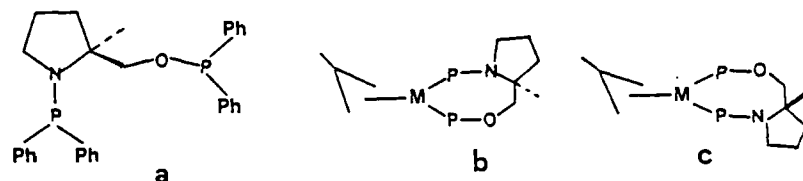
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**Stereochemical studies of  $\eta^3$ -allylPd(II) complexes containing chiral chelating ligand.**

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Pd-mediated asymmetric allylation, leading to selective C-C bond formation is a reaction of primary importance in organic chemistry. Despite the relevant number of studies and applications reported, the systematic outcome of the reaction is not defined and the control of asymmetric induction together with the rise in optical yields are far from optimal. In order to offer an insight into the correlation between precursor, intermediate and product in "real-like" conditions, we illustrate the solution characterization of  $[\eta^3\text{-C}_4\text{H}_7\text{PdLL}']\text{X}$  (where LL' = chiral chelating ligand with symmetry lower than C<sub>2v</sub>). The structures of the ligand (S)-N-(diphenylphosphino)-2-diphenylphosphinoxymethylpyrrolidin (herein abbreviated as ((S)-Prolophos)) and of the two diastereoisomeric forms of the complex  $\{\eta^3\text{-C}_4\text{H}_7\text{Pd}((\text{S})\text{-Prolophos-PP}')\}^+\text{X}^-$ , 1, are shown in formulae a, b, c, respectively.



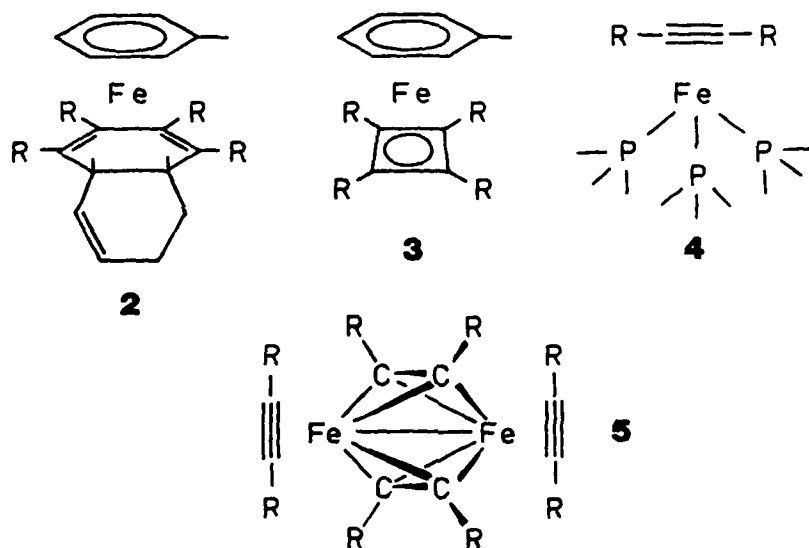
The full characterization of both the ligand and the complex 1 have been performed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  one- and two-dimensional n.m.r. techniques. On the basis of the n.m.r. findings, the absolute configuration of the two diastereoisomers has been assigned (i.e. the major and minor isomers have structure b and c, respectively). The comparative values of  $^3J(\text{XP})$  (where X = allylic carbon, proton) allow an evaluation of the relative *trans* influence of the two phosphorus atoms indicating that -PN- is a better  $\sigma$  donor than -PO-. The analysis of the relative  $^{13}\text{C}$  shifts of the allylic carbons suggests that -PO- is a stronger  $\pi$  acceptor than -PN-. On the basis of these results, hypotheses on the regioselectivity of the nucleophilic attack on the coordinated allyl are formulated.

This work was supported by the C.N.R. (Centro di studi sulla sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione, Milano, Italy).

NEW ROUTES TO  $\pi$ -COMPLEXES OF IRON  
VIA CYCLOTRIMERIZATION OF ALKYNES

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(Toluene)bis(ethene)iron 1 is rapidly accessible in good yield via a metal vapor reaction. It cyclotrimerizes alkynes  $RCCR'$  ( $R, R' = H$ , alkyl, phenyl, alkylester) below room temperature. We use the catalytic cycle as a generator of highly reactive complexes, which may be trapped by suitable reagents such as phosphites, olefines or dienes. The reactions of 1 with diphenylacetylene or bis(trimethylsilyl)acetylene directly yield new  $\pi$ -complexes of iron. Examples for the many products are the compounds 2-5.



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AMINO-COPPER COMPLEXES AS CATALYSTS FOR  
ADDITION REACTION

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Copper complexes prepared under homogeneous conditions "in situ" from copper I chloride and aliphatic primary amine in excess of  $\text{CCl}_4$  were compared with those immobilized on the surface of organic polymer support. As polymerous carriers macroporous 2,3-epoxypropylmethacrylate copolymer crosslinked by ethylenedimethacrylate or copolymers of styrene and divinylbenzene both modified by built-in primary amino groups were used.

The rate constant of addition reaction (at  $70^\circ\text{C}$ ) between  $\text{CCl}_4$  and styrene giving 1,3,3,3-tetrachloropropylbenzene was used as a measure of catalytic activity of prepared complexes.

$$d|\text{Prod.}|/dt = k \times |\text{Styr.}| \times |\text{Cat.}|_0$$

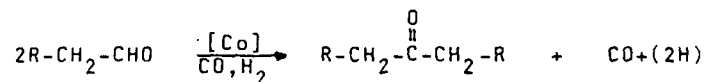
The concentration of styrene and that of copper complex was 0.77 Mol/L and 0.06 Mol/L, respectively.

The activity of catalytic complex depends on the molar ratio of copper and amine group in complex. Under homogeneous conditions the most active complex was obtained from  $\text{CuCl}$  and n-butylamine in ratio 1:2. Supported copper complex pretreated by primary amine decreases its activity as a reason of wash-off of a small part of Cu from supported complex and a rearrangement of amino groups in retained complex. For immobilized copper complexes the dependency of activity on the structure and surface of carrier and on the content of amino groups in polymerous matrix was characterized.

NOVEL ACCESS TO KETONES BY CATALYTIC COUPLING  
OF ALDEHYDES

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Although a number of transition-metal complexes activate aldehydes to lead either to decarbonylation or to hydroacylation reactions in the presence of olefins, no direct formation of ketones seems to have been reported. We now describe a straightforward catalytic synthesis of ketones from aldehydes, a reaction that globally involves the formation of a C-C bond as well as the loss of one molecule of carbon monoxide :



Pressure as well as the presence of basic ligands was crucial for the obtention of ketones. For example, a solution of phenylacetaldehyde at 150° in the presence of a catalytic amount of cobalt carbonyl under 10 MPa of CO-H<sub>2</sub> yielded 1,3-diphenyl-2-propanone (dibenzylketone, >70%). Benzaldehyde did not react under the same reaction conditions. Hydroacylation of an olefin intermediate was ruled out as a major reaction pathway.

Some Reminiscences

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"In his last public lecture Professor Wilkinson is expected to talk about his early days in organometallic chemistry and to report on some recent work on rhenium and platinum homoleptic alkyls and aryls".



# COMPETITIVE UNCATALYZED GEOMETRICAL ISOMERIZATION AND $\beta$ -HYDRIDE ELIMINATION OF ALKYL COMPLEXES OF PLATINUM(II).

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Rates and activation parameters for the spontaneous cis to trans isomerization of monoalkyl  $[\text{Pt}(\text{PEt}_3)_2(\text{R})\text{Cl}]$  (  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_2\text{D}_5$ ,  $n\text{-C}_3\text{H}_7$ ,  $n\text{-C}_4\text{H}_9$ ,  $\text{CH}_2\text{Si}(\text{CH}_3)_3$  ) complexes have been measured in isopropanol. The reactions are inhibited by chloride ion and for all systems the isomeric equilibrium lies well to the side of the trans form. As in the case of the related aryl complexes, the isomerization mechanism involves dissociative loss of chloride and interconversion of two T-shaped  $[\text{Pt L}_2(\text{alkyl})]^+$  3-coordinate intermediates. An incipient interaction of the  $\beta$ -hydrogens of the alkyl group with the metal in the transition state leading to the first platinum cation intermediate accounts for the much higher reactivity of complexes in which  $\text{R} = \text{Et}$ ,  $n\text{-Pr}$  and  $n\text{-Bu}$  with respect to that of complexes containing alkyl groups with no  $\beta$ -hydrogens.

The  $n$ -propyl and  $n$ -butyl derivatives, in addition to spontaneous isomerization undergo thermal decomposition through a concurrent pathway yielding trans- $[\text{Pt}(\text{PEt}_3)_2\text{HCl}]$  and olefins ( propene and 1-butene, cis-2-butene and trans-2-butene in the ratio 1: 1: 0.04, respectively). No alkanes are produced in these reactions that go to completion and are unaffected by the presence of excess of chloride ion in solution. The relative rates of the two competing processes either in the neat solvent or in solutions containing chloride have been calculated through kinetic, spectrophotometric and GLC measurements. The most probable mechanism for the thermolysis involves a nondissociative pathway in which the loss of olefin after facile reversible  $\beta$ -hydride elimination is probably rate determining.

REACTIVITY OF A CATIONIC OSMIUM POLYHYDRIDE  
TOWARDS ETHYLENE

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Alamos National Laboratory, Los Alamos, NM (U.S.A.)

We have established, by neutron diffraction, that  $\text{FeH}_4(\text{PEtPh}_2)_3$  contains two hydride ligands and one dihydrogen molecule.  $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ , in contrast, contains four hydride ligands. In order to explore further this difference, we have protonated  $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$  to give  $\text{OsH}_5(\text{PMe}_2\text{Ph})_3^+$ , which reacts with ethylene (1 atm, 25°) to give *cis,mer*- $\text{OsH}(\text{C}_2\text{H}_4)_2(\text{PMe}_2\text{Ph})_3^+$ . Multinuclear NMR studies, including work with  $^{13}\text{C}_2\text{H}_4$ , reveals this ion to have chemically-inequivalent ethylene ligands. The  $\text{C}_2\text{H}_4$  *trans* to a phosphine shows rigidity of the  $\text{OsC}_2$  plane, while that *trans* to hydride shows rapid olefin rotation. Detailed studies of these and related dynamic processes, including attempted olefin hydrogenation, will be reported, as well as attempts to establish the possible presence of intact  $\text{H}_2$  in  $\text{OsH}_5(\text{PMe}_2\text{Ph})_3^+$ .

## NEW REACTIONS OF IODO-RUTHENIUM(0) NUCLEOPHILES

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Ruthenium(II) forms very stable complexes with several  $N,N'$ -chelating ligands. The reduction of  $[(N--N')Ru(CO)_2I_2]$  1 leads to the pentacoordinate anion  $[(N--N')Ru(CO)I]^-$  2 [1], which undergoes a number of low temperature nucleophilic reactions, e.g. with alkyl halides and triflates, allyl halides and triflates, silyl halides, ammonium salts (as proton source), acyl halides etc. The oxidative addition products always contain the iodo ligand. The conformationally stable and kinetically inert complexes  $[(N--N')Ru(CO)_2(Y)I]$  3 allow the comparison of many electrophiles Y at the same center. Starting from diolefin complexes  $[N--N')Ru(diene)Cl_2]$  [2] analogues  $[(N--N')Ru(diene)I]^-$  4 have also been prepared and reacted with electrophiles.

Reduction of complexes 3 ( $Y = -CH_3$ ;  $N--N' = \text{i}pr\text{-DAD} = \text{i}pr\text{-N=CH-CH=N-i}pr$ ) gives a Ru-Ru bonded dimer  $[(N--N')(CO)_2Ru-Ru(CO)_2(N--N')]$  5. For another complex 3 ( $Y = I^-$ ) the same type of Ru-Ru bonding occurs for bulky  $(N--N')$ , while for the relatively small  $\text{i}pr\text{-DAD}$  the known Ru(0) dimers  $[(DAD)Ru(CO)_2]_2$  [3] are formed. Complex 5 shows an exceptionally strong CT absorption band near the infrared. Kinetic results from electrochemical studies are presented to illustrate the reactivity of the Ru(II), Ru(I), and Ru(0) species

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FACTORS AFFECTING THE EQUILIBRIUM CONSTANT OF  
HOMOLYSIS OF COMPLEXES WITH METAL-CARBON  $\sigma$  BONDS IN  
AQUEOUS SOLUTIONS: PULSE RADIOLYSIS STUDIES.

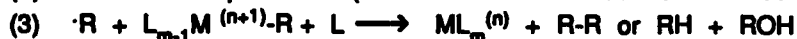
Dan Meyerstein

R. Bloch Coal Research Center and Chemistry Department  
Ben Gurion University of the Negev, Beer-Sheva, Israel.

Aliphatic free radicals,  $\cdot R$ , react with a large variety of transition metal complexes to form transient complexes with metal-carbon  $\sigma$  bonds. Recently it was observed that the mechanism of decomposition of these complexes involves in many systems the homolysis of the metal-carbon  $\sigma$  bond:



The homolysis reaction is followed by one of the following reactions:



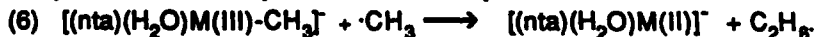
The equilibrium constant  $K_1$  can be determined by studying the dependence of the rate of formation of  $L_{m-1}M^{(n+1)}-R$  on  $[ML_m^{(n)}]$ , by studying the dependence of the absorption due to  $L_{m-1}M^{(n+1)}-R$  on  $[ML_m^{(n)}]$  or by studying the dependence of the rate of decomposition of  $L_{m-1}M^{(n+1)}-R$  on  $[S]$  when  $k_2$  is known.

The technique enables the study of the effect of the nature of the central cation  $M$ , the ligands  $L$  and substituents on  $R$  on  $K_1$ . Specific examples for each effect and mechanism will be discussed, these examples include:

The determination of the equilibrium constant  $K_5$  for  $M = Mn, Fe$  and  $Co$ .



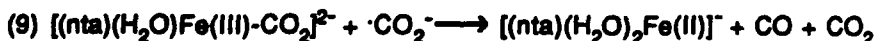
in this system the homolysis is followed by



whereas reaction (7)



is followed by



For  $M = Co$  the effect of substituents on the methyl on  $K_5$  is reported.

Other systems discussed will include those in which  $ML_m^{(n)} = Cr_{aq}^{2+}$ ,  $Cu_{aq}^{+}$ ,  $Cu(II)$ tetrasulfophthalocyanine and  $Ni(II)$ tetrasulfophthalocyanine.

SUBSTITUENT EFFECTS ON THE RATES OF CO SUBSTITUTION  
OF  $(\eta^5\text{-C}_5\text{H}_4\text{X})\text{Rh}(\text{CO})_2$

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The syntheses and characterization of the new compounds  $(\eta^5\text{-C}_5\text{H}_4\text{CF}_3)\text{Rh}(\text{CO})_2$  and  $(\eta^5\text{-C}_5\text{H}_4\text{N}(\text{CH}_3)_2)\text{Rh}(\text{CO})_2$  are reported. The compounds  $(\eta^5\text{-C}_5\text{H}_4\text{X})\text{Rh}(\text{CO})_2$  and  $(\eta^5\text{-C}_5\text{H}_4\text{X})\text{Rh}(\text{CO})\text{PPh}_3$  (where X = H, NO<sub>2</sub>, CF<sub>3</sub>, Cl, CH<sub>3</sub>, or N(CH<sub>3</sub>)<sub>2</sub>) show a good linear correlation between the values of CO stretching frequencies,  $\nu_{\text{CO}}$ , and the Hammett  $\sigma$  values of the X ring substituents. This may be the first time such a correlation has been reported, and it is believed to mirror the electron density on the metal which in turn results in greater or lesser back  $\pi$ -bonding, M  $\rightarrow$  CO. In spite of this the rates of CO substitution of these compounds show strong deviations from linear correlation with Hammett  $\sigma$  values. This is rationalized in terms of resonance stabilization of the transition state for reaction by certain ring substituents.

We are now collaborating with Professor Dennis L. Lichtenberger on a core and valence ionization study<sup>1</sup> of these compounds in an attempt to determine the separate contributions of the  $\sigma$  and the  $\pi$  effects of the ring substituents on the rates of CO substitution.

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LARGE AND SMALL DEUTERIUM KINETIC ISOTOPE EFFECTS  
IN INTRAMOLECULAR PROCESSES IN TRANSITION METAL HYDRIDES

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We have previously reported a small primary deuterium kinetic isotope effect ( $kH/kD \sim 1.5$ ) in various intramolecular rearrangements<sup>1</sup> and chemical reactions.<sup>2</sup> We have now found that this small isotope effect is not confined to polynuclear metal hydrides but is also observed in intramolecular rearrangements involving hydride motion in mononuclear species (e.g.  $[(\eta-C_6H_5)Cr(CO)_2(P(CH_3)_2C_6H_5)H]^+$ ). In addition, we have applied the small isotope effect to understanding the connectivity between hydride motion and migrations of other ligands in the cluster systems  $(\mu-H)_2M_3(CO)_9(\mu_3-S)$  ( $M = Ru, Os$ ) and  $(\mu-H)_2Os_3(CO)_9(\mu_3-alkyne)$ .

We have also previously documented a large isotope effect ( $kH/kD > 50$ ) in the intramolecular ligand to metal hydrogen transfer involved in the conversion of  $(\mu-H)(\mu-COH)M_3(CO)_{10}$  to  $H(\mu-H)M_3(CO)_{11}$  ( $M = Ru, Os$ )<sup>3</sup> We have now documented a large isotope ( $kH/kD = 6$ ) for the intramolecular metal to ligand hydrogen transfer involved in the conversion of  $H(\mu-H)Os_3(CO)_{10}(CNR)$  ( $I, R = CH_3$ )  $(\mu-H)Os_3(CO)_{10}(\mu-\eta^1-C-N(H)R)$ . This isotope effect is not observed in the conversion of  $I(R = C_6H_5)$  to the isomeric  $(\mu-H)Os_3(CO)_{10}(\mu-\eta^2-CH=NR)$  where a small inverse isotope effect is observed. The temperature dependence of these isotope effects will be discussed as a means of evaluating the barrier tunnelling component in these types of chemical reactions.

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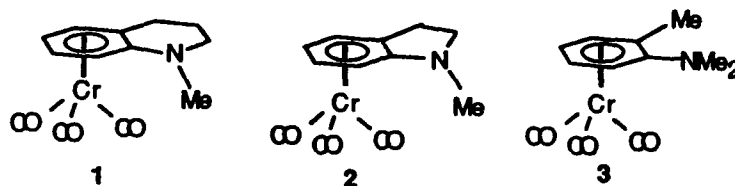
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# Reversible Addition of Carbon Nucleophiles to some Nitrogen-Substituted $\eta^6$ -Arenetricarbonylchromium(0) Compounds

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The nucleophilic addition/oxidation reactions of  $\eta^6$ -1-methyl-1,2,3,4-tetrahydroquinoline-tricarbonylchromium(0) **1**,  $\eta^6$ -1-methylindolinetricarbonylchromium(0) **2**, and  $\eta^6$ -2-N,N-dimethylaminotoluenetricarbonylchromium(0) **3** with the nucleophiles 2-lithio-2-methylpropionitrile **A**, 2-lithioacetonitrile **B** and 2-lithio-2-methyl-1,3-dithiane **C** have been studied.



The regioselectivity in the addition of stabilized nucleophiles is time- and temperature-dependent indicating the onset of thermodynamic control in prolonged/high temperature reactions. The addition is reversible according to crossover experiments with  $\text{benzeneCr(CO)}_3$ , the rate for dissociation of the C-C bond being strongly dependent on both the structure of the intermediate  $\eta^5$ -cyclohexadienyltricarbonylchromium anions as well as the structure of the nucleophile. The regioselectivity of the thermodynamically controlled reaction of **2** has been correlated with the relative energies obtained from EHT calculations on a model system for the intermediate cyclohexadienyltricarbonylchromium anions.

The regioselectivity of the addition/oxidation reaction can be optimized by the proper choice of reaction conditions for each of the compounds **1**, **2** and **3**.

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Photochemically induced C-H Activation Using  
 $(\eta^3\text{-C}_3\text{H}_3)\text{Rh}(\text{PMe}_3)\text{C}_2\text{H}_4$  - A Mechanistic Study

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The work of Bergman, Jones and Graham has shown that efficient C-H activation of arenes/alkanes may be achieved with the reactive 16e intermediates  $(\eta^3\text{-C}_3\text{R}_3)\text{ML}$  ( $\text{R} = \text{H}, \text{CH}_3$ ;  $\text{M} = \text{Rh}, \text{Ir}$ ;  $\text{L} = \text{PMe}_3, \text{CO}$ ) via photo-ejection of  $\text{H}_2$ , CO from their 18e precursors<sup>1</sup>. We have now utilised the photo-lability of  $\text{C}_2\text{H}_4$  in  $\text{CpRhL}(\text{C}_2\text{H}_4)$  complexes<sup>2</sup> to examine the mechanisms of these reactions more closely. Here we report investigations of the photo-chemistry of  $\text{CpRhPMe}_3(\text{C}_2\text{H}_4)$  in solution, in low temperature matrices and by laser flash photolysis.

Photolysis of  $\text{CpRhPMe}_3(\text{C}_2\text{H}_4)$  in aromatic solvents yields stable aryl hydride complexes via elimination of  $\text{C}_2\text{H}_4$  and oxidative addition of solvent C-H bonds. In alkanes, C-H activation occurs unselectively to give thermally unstable alkyl hydride complexes characterised by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r.. The reaction intermediate,  $\text{CpRhPMe}_3$ , remains elusive even at 20K in an argon matrix, where intramolecular C-H activation of co-ordinated  $\text{PMe}_3$  (cyclometallation) is dominant. The cyclometallated product exhibits a conspicuous  $\nu(\text{Rh-H})$  band at ca.  $2040\text{ cm}^{-1}$  in the i.r.. Laser flash photolysis of  $\text{CpRhPMe}_3(\text{C}_2\text{H}_4)$  in alkane solvents fails to show any transients, only products. However, a transient is observed in arene solvents which is assigned to  $\text{CpRhPMe}_3(\eta^2\text{-arene})$ . Evidence for such intermediates has been published by Jones<sup>3</sup>. The rate of isomerisation of  $\text{CpRhPMe}_3(\eta^2\text{-C}_6\text{H}_6)$  to  $\text{CpRhPMe}_3(\text{C}_6\text{H}_5)(\text{H})$  is  $1 \times 10^3\text{ s}^{-1}$ .

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3. W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 1984, **106**, 1650.

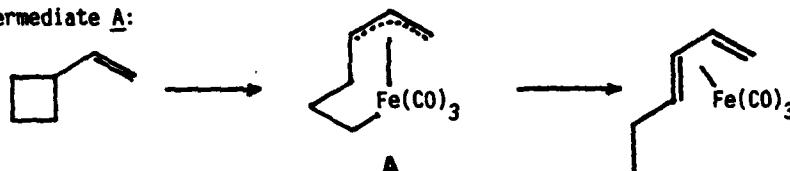


## IRON CARBONYL INDUCED REARRANGEMENT OF VINYL-CYCLOBUTANE SYSTEMS

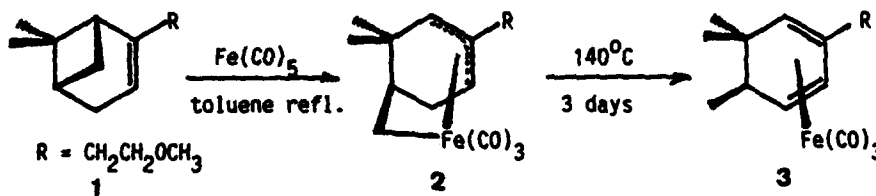
Titus A. Jenny, Institut de chimie organique, Université de Fribourg,  
CH-1700 Fribourg, Switzerland

Although facile ring opening of vinylcyclopropanes by the action of iron carbonyls has long been known, only one report appeared so far on the corresponding behaviour of vinylcyclobutanes<sup>1</sup>.

We found now, that vinylcyclobutanes can be reacted with  $\text{Fe}(\text{CO})_5$ , either thermally at temperatures above  $100^\circ\text{C}$ , or photochemically at temperatures above  $60^\circ\text{C}$ , to yield products which are derived from the expected  $\pi$ -allyl complexed intermediate A:



Surprisingly, intermediates of the type A can be isolated as major products, if the substituents and further ring connections of the reacting vinylcyclobutane systems lead to products which meet the steric requirements of complexation on iron:



Thus, starting from enantiomerically pure nopol methylether 1, one obtains with complete steric control the highly versatile complex 2 as a slightly air sensitive, stable compound in moderate yield. Hydrogen transfer on subsequent heating leads to the substituted 1,3-cyclohexadiene complex 3, without loss of enantiomeric purity.

## References

- 1) A. Stockis and E. Weissberger, J. Am. Chem. Soc., (1975), 97, 4288.

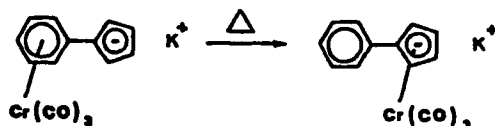
THE MIGRATION OF  $\text{Cr}(\text{CO})_3$  FROM THE PHENYL TO THE  $\sigma$ -BONDED CYCLOPENTADIENYL RING IN 9-PHENYL-FLUORENYL, 3-PHENYL-INDENYL, AND PHENYL-CYCLOPENTADIENYL ANIONS.

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Centro Studi Stati Molecolari, Radicalici ed Eccitati del  
CNR, Via Loredan, 2 - 35131 PADOVA (Italy)

Intramolecular haptotropic rearrangements in biphenyl or in iso-electronic systems have not been previously observed. Recently, the migration of  $\text{Cr}(\text{CO})_3$  occurring between co-ordinative sites separated by a carbon-carbon  $\sigma$  bond has been shown by us to occur in the 3-phenyl-pentadienyl anion.<sup>1</sup>

In this communication we will show that the migration of  $\text{Cr}(\text{CO})_3$  in the phenyl-cyclopentadienyl anion



takes place irreversibly in the temperature range 325±342 K. Analogous shift of the inorganic unit occurs also in the 9-phenyl-fluorenyl and the 3-phenyl-indenyl anions. The rates and the activation parameters of these processes are compared with those of other haptotropic rearrangements.

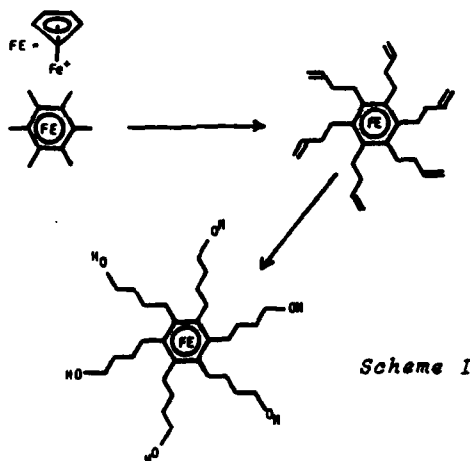
<sup>1</sup> A. Ceccon, A. Gambaro, A. Venzo, J. Chem. Soc. Chem. Commun., (1985) 540

## Tentacled Iron Sandwiches

Françoise Moulines and Didier Astruc

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 Université de Bordeaux I, 351, cours de la Libération, 33400 Talence,  
 France.

The perfunctionalization of  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_6\text{H}_6)]^+ \text{PF}_6^-$  has been achieved<sup>1</sup> by reaction with allylbromide and *t*-BuOK in THF. (scheme I) This reaction follows the known permethylation reaction with  $\text{CH}_3\text{I}$ <sup>2</sup>. The reactivity of the double bonds has been investigated with the aim to design new discoid molecules.



Scheme I

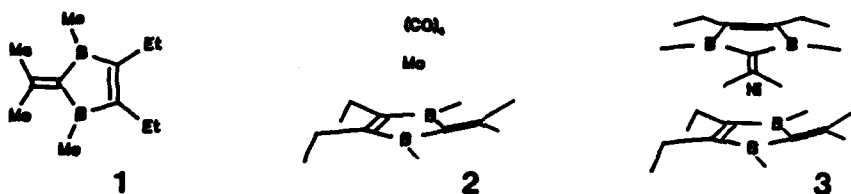
1 F. Moulines, D. Astruc submitted to *Angew. Chem. Int. Ed. Engl.*

2 J.-R. Hamon, J.-Y. Saillard, A. Le Beux, M. McGlinchey, D. Astruc,  
*J. Am. Chem. Soc.* 1982, **104**, 7549-7555.

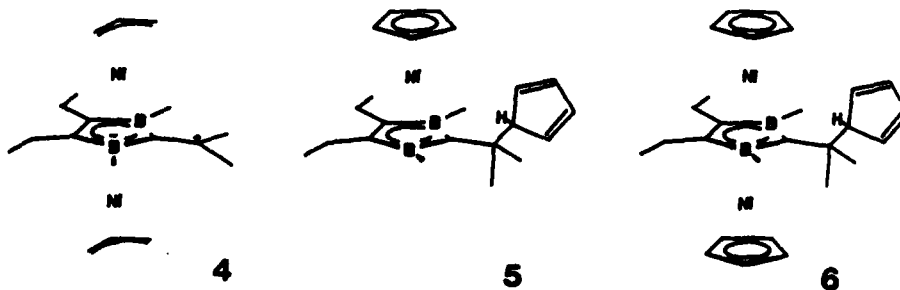
METAL COMPLEXES OF 1,3-DIHYDRO-  
1,3-DIBORAFULVENE DERIVATIVES

Walter Siebert, Volker Schäfer, Gregor Brodt and Hans Pritzkow,  
Anorganisch-Chemisches Institut der Universität, Im Neuenheimer  
Feld 270, D-6900 Heidelberg, FRG

Reaction of (Z)-bis(dichloroboryl)hexene-3 with 1,1-bis(trimethylstannyl)-2-methyl-1-propene leads to of the diborafulvene derivative **1**. This Lewis acidic heterocycle is a four-electron donor and it has good acceptor properties for the formation of mononuclear and dinuclear complexes. A typical example is the tetracarbonylmethyl complex **2**, which is obtained on reaction of **1** with



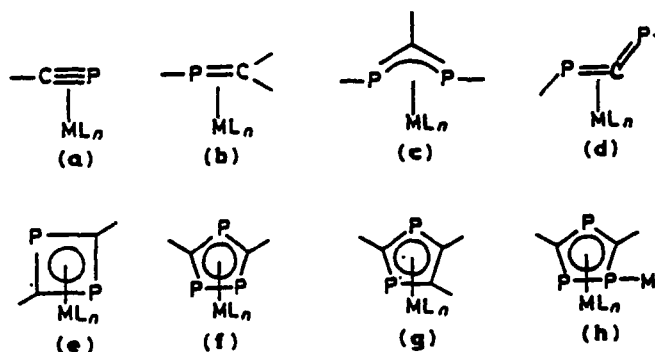
$\text{Mo(CO)}_4$ . With bis(allyl)nickel the sandwich **3** and the triple-decker **4** are formed. An unusual transfer of  $\text{C}_5\text{H}_5$  occurs when **1** is reacted with  $[(\text{C}_5\text{H}_5)\text{Ni(CO)}]_2$  to give **5** and the paramagnetic triple-decker sandwich **6**.  $[(\text{C}_5\text{H}_5)\text{Fe(COD)}]_2\text{Zn}$  and **1** yield paramagnetic FeFe triple-decker complexes. The structure of several complexes will be discussed.



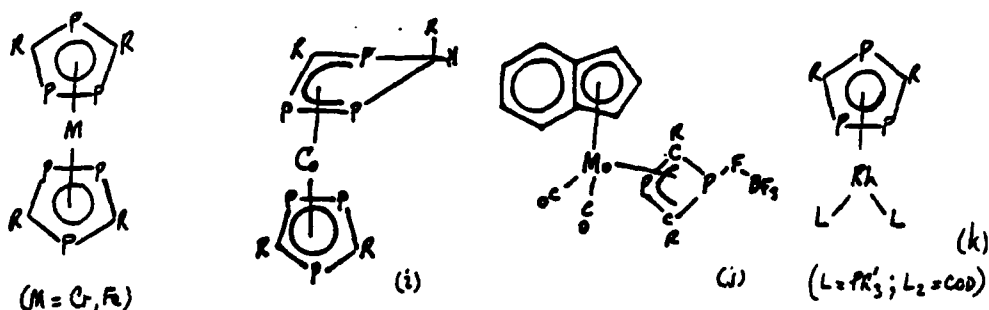
1) V. Schäfer, H. Pritzkow, W. Siebert, Angew.Chem. **100** (1988) 272

John F. Nixon, Rainer Bartsch, Mohd. Jamil Maah and Peter B. Hitchcock,  
School of Chemistry and Molecular Sciences, University of Sussex,  
Brighton, BN1 9QJ, Sussex, England.

There is considerable current interest in the ligating behaviour of unsaturated organophosphorus ligands.<sup>1</sup> It has become increasingly apparent that formal replacement of a CH fragment by P or a CH<sub>2</sub> fragment by PR in organic compounds can lead to a variety of novel unsaturated organophosphorus compounds, many of which form complexes with transition metals. During the past few years the structural types (a)–(h) have been established (ML<sub>n</sub> = transition metal and attendant ligands):



Recent results in syntheses, photo-electron spectra and electrochemistry of sandwich compounds of the type  $[\text{M}(\eta^5\text{-P}_3\text{C}_2\text{R}_2)_2]$ , (M = Cr, Fe), will be reported. New ring systems typified by (i) and (j)<sup>†</sup> below (the former containing a 1,2,4 triphospha-butadiene) will be described as will "half-sandwich" compounds (k), (l–g<sub>4</sub>).



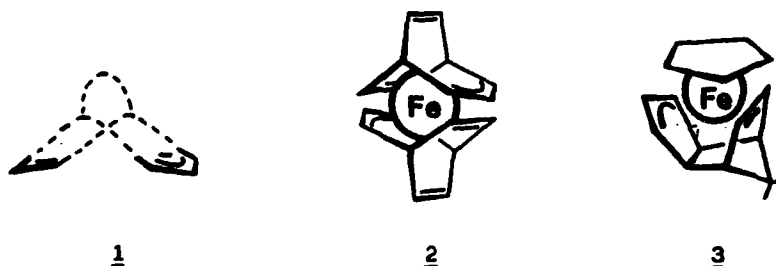
1. J. F. Nixon Chem. Revs. In Press.

<sup>†</sup> In collaboration with Prof. M. Green, King's College, London.

ANALOGUES OF METALLOCENES WITH SEPARATED  
ALLYL AND OLEFIN SYSTEMS

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Carbanions of type 1 play an important role in the discussion of homoaromaticity<sup>1</sup>. As a working base we regard 1 as a cyclopentadienyl (Cp) the  $\pi$ -system of which has been broken down into an olefinic and an allylic system so that corresponding transition metal complexes of 1 show increased reactivity as compared to Cp complexes. We describe the synthesis of complexes containing the following ligands: bicyclo[3.2.1]octa-2,6-dien-4-yl, bicyclo[3.2.2]nona-2,6,8-trien-4-yl, and tricyclo[5.2.1.0<sup>2,6</sup>]deca-3,8-dien-5-yl. Two examples, 2 and 3, are shown below. Compared with ferrocene these complexes display some remarkable differences and similarities which will be discussed.

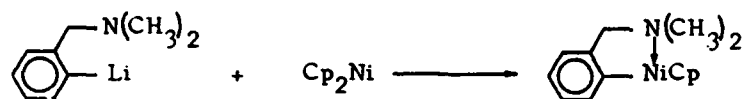


1 a) L. A. Paquette, *Angew. Chem.* 90(1978)114. b) R. Lindh, B. O. Roos, G. Jönvall, P. Ahlberg, *J. Am. Chem. Soc.* 108(1986)6554 and references cited therein.

# SYNTHESIS AND REACTIONS OF CYCLOMETALLATED COMPOUNDS OF NICKEL

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Institute of Organic Technology, Warsaw Technical University,  
Koszykowa 75, 00-662 Warsaw, Poland

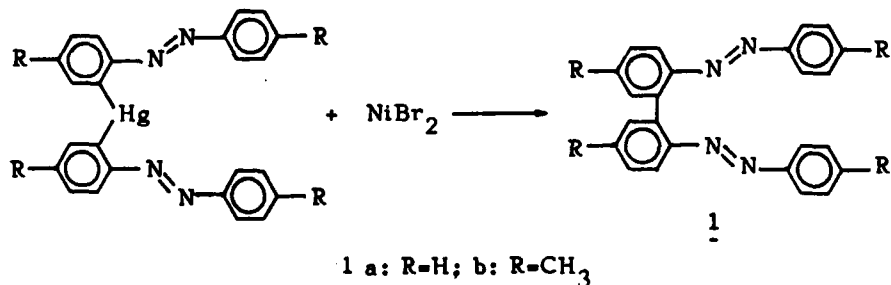
Treatment of bis-cyclopentadienylnickel with 2-((dimethylamino)methyl)phenyllithium in THF at room temperature for 2 h leads to the formation of  $\eta^5$ -cyclopentadienyl(2-((dimethylamino)methyl)phenyl)nickel with 60% yield.



The product was recrystallized from hexane and characterized by elemental analysis and  $^1\text{H}$  NMR:  $/\text{CDCl}_3/$  6.86 /m, 4H, ring H/, 5.20 /s, 5H, Cp ring H/, 3.61 /s, 2H,  $\text{CH}_2/$ , 2.50 /s, 6H,  $\text{NCH}_3/$ .

Neither this compound nor its azobenzene analogue insert olefins and dienes. The reaction of  $(\text{azb})\text{NiCp}$  with  $\text{Cl}_2\text{C}=\text{CCl}-\text{CCl}=\text{CCl}_2/\text{H}_2\text{O}$  mixture leads to the formation of 2-hydroxyazobenzene.

The reaction of bis-((2-aryloxy)aryl)mercury with nickel bromide in THF leads to the coupling of (aryloxy)arene groups in ortho positions.



After recrystallization from pentane compounds 1a and 1b were isolated with 52% and 62% yield respectively and were characterized by means of elemental analysis, IR and mass spectra.

CYCLOOCTATETRAENE AS BRIDGING LIGAND: STRUCTURES, DYNAMIC BEHAVIOUR AND REDOX CHEMISTRY OF DIMETALLIC COMPLEXES

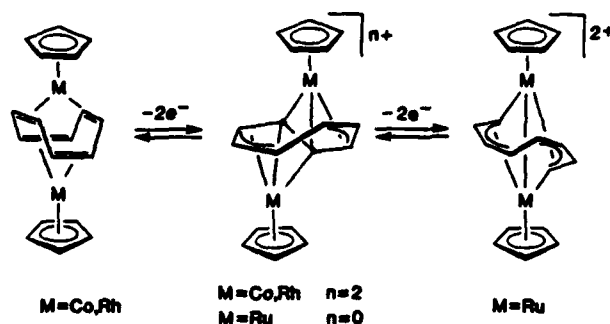
Albrecht Salzer and Urs Ruppli, Anorganisch-chemisches Institut der Universität Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland

Joseph Edwin and William E. Geiger, Department of Chemistry, University of Vermont, Burlington, Vermont, 05405

Arnold L. Rheingold, Department of Chemistry, University of Delaware, Newark, Delaware 19716

A series of dimetallic complexes of general composition  $[\text{Cp}_2\text{M}_1\text{M}_2(\mu\text{-C}_8\text{H}_8)]^{n+}$  will be presented with  $\text{M}_{1,2} = \text{Co}, \text{Rh}, \text{Ru}$  and  $n = 0, 1, 2$ .

$\text{Cp}_2\text{Rh}_2\text{C}_8\text{H}_8$  occurs as two isomers with either cis or trans coordination to the bridging  $\text{C}_8\text{H}_8$  moiety. Both complexes undergo reversible two-electron oxidations with concomitant structural rearrangements. The trans-dication shows an unusual slipped tripledecker structure.



In search for more electron-deficient members of this series, the oxidation of  $\text{Cp}_2\text{Ru}_2\text{C}_8\text{H}_8$ , also a slipped tripledecker, was investigated. This also undergoes reversible two-electron oxidation. In the dication the eight-carbon ring of the neutral precursor has opened, giving a chain whose termini now bridge a newly formed Ru-Ru bond. The central structure is basically a ten-membered dimetallacyclic ring. This reaction appears to be the first example of a reversible ring opening of a bridging olefinic ligand.

A. Salzer, U. Ruppli, J. Edwin, W. E. Geiger and A. L. Rheingold, J. Am. Chem. Soc. (1987) 109, 7893



**The Chemistry and Structures of Trimesitylaluminum Derivatives; Novel  
Sterically Hindered Organometallic Compounds**

John P. Oliver, Sreeni De Mel, and Mark LaLama

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

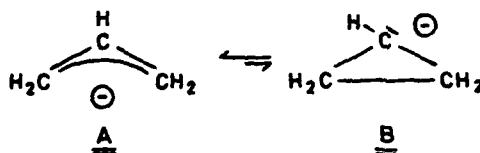
The structure of the sterically crowded molecule, trimesitylaluminum, determined previously,<sup>1</sup> will be compared with the crystal structure of trimesitylaluminum•THF(1) adduct which has been determined by single crystal X-ray diffraction techniques. The latter compound crystallizes in the monoclinic lattice system, space group  $P2_1/c$ , with unit cell dimensions of  $a = 8.457(7)$ ,  $b = 14.318(2)$ ,  $c = 22.234(3)$  Å,  $\beta = 98.271(9)^\circ$ ,  $v = 2264.48(49)$  Å<sup>3</sup> and  $Z = 4$ . The final full matrix least-squares refinement on 2062 data gave  $R = 7.5\%$  and  $R_w = 4.5\%$ . 1 is similar to other organoaluminum adducts yielding a four-coordinate aluminum atom but the steric crowding leads to a slightly longer Al-C distances,  $d_{av} = 2.017$  Å and an Al-O distance of  $1.969(5)$  Å, significantly longer than the Al-O distance observed in other THF and diethyl ether adducts. Further evidence of the steric crowding is seen in the distortion of the C-Al-O angles with one of these angles  $91.4^\circ$ , far less than observed in other ether adducts of triorganoaluminum derivatives. Simple calculations on the "acceptor" site size will be discussed and their implications with regard to the formation of other adducts will be discussed and compared with experimental results. The formation and structure of derivatives in which one or more alkoxide or halide groups have been substituted for a mesityl group will be described.

- 1) Synthesis, Molecular Structure, and NMR Spectra of Trimesitylaluminum, A Novel Three-Coordinate Molecule: John J. Jerius, Juliet M. Hahn, A. F. M. Maqsudur Rahman, Ole Mols, William H. Ilseley, and John P. Oliver, *Organometallics*, 1986, 5, 1812-14.

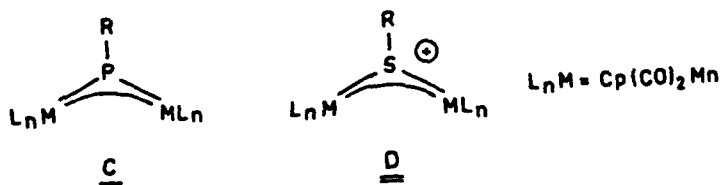
VALENCE TAUTOMERISM OF RX-BRIDGED  
(X = P.. Sb, S.. Te) DIMETAL COMPOUNDS

Gottfried Huttner, Anorganisch-Chemisches Institut der Universität Heidelberg  
Im Neuenheimer Feld 270, D - 6900 Heidelberg, F.R.G.

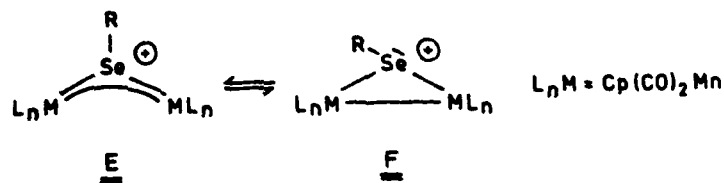
The allylic anion A and its ring closed valence tautomere B, the cyclopropyl anion, are close and interconvertible neighbours on the corresponding hyper-surface.



The behaviour of these master compounds is mimicked by their organometallic analogues such as phosphinidene (C) or "sulfinidene" (D) complexes.



The Selenium homologue of D, E, displays a temperature dependent equilibrium between the open (E) and the closed form F.

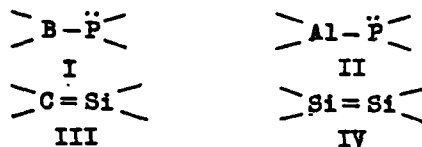


The observation itself and its implications are discussed.

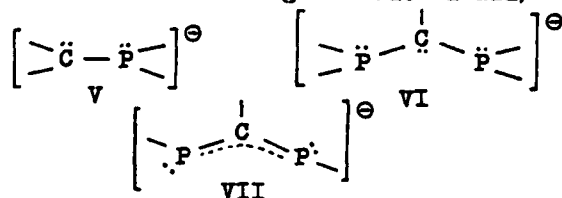
## NOVEL "III/V"-COMPOUNDS

Hans H. Karsch, G. Hanika, A. Schneider, G. Müller  
 Anorganisch-chemisches Institut, Technische Universität München,  
 Lichtenbergstr. 4, D-8046 Garching, F.R.G.

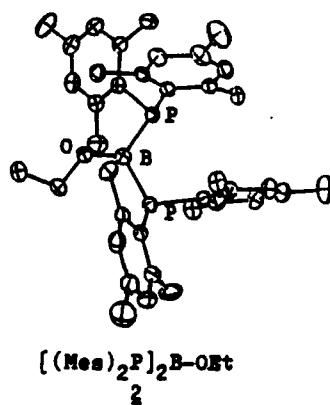
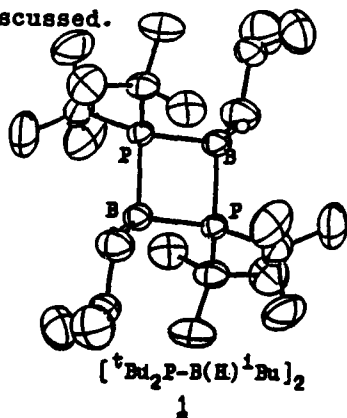
Taking advantage of the concept of isoelectronic relationship, "III/V"-analogues (I, II) of silenes (III) and disilenes (IV) may be anticipated.



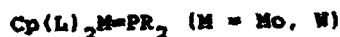
Monomeric, dimeric and trimeric derivatives of (I, II) with more or less bulky substituents have been prepared and characterized structurally and/or spectroscopically. Other anionic phosphorus based ligands than diorganophosphides ( $\text{R}_2\text{P}^-$ ), e.g. (V), (VI) and (VII) likewise give neutral III/V compounds.



Examples for dimeric and monomeric boron diorganophosphides are 1 and 2, respectively. Preparation, properties and structures are discussed.



## FUNCTIONAL AND CHIRAL PHOSPHORUS METAL DOUBLE BOND COMPLEXES



Wolfgang Malisch, S. Amann, E. Nödes, U. Hirth and M. Schmeuß, Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG

Functional metal phosphorus double bond complexes  $\text{Cp}(\text{CO})_2\text{M}=\text{P}(\text{R})\text{X}$  (1) ( $\text{X} = \text{H}, \text{Cl}$ ;  $\text{R} = \text{alkyl}, \text{aryl}, \text{alkoxy}, \text{dialkylamino}$ ;  $\text{M} = \text{Mo}, \text{W}$ ) can be synthesized either via decarbonylation of the corresponding metallo-phosphanes  $\text{Cp}(\text{CO})_3\text{M}-\text{P}(\text{R})\text{X}$  (2) or via the dehydrochlorination of the bifunctional phosphane complexes  $\text{Cp}(\text{CO})_2\text{M}(\text{Cl})-\text{P}(\text{H})(\text{R})\text{X}$  (3). In special cases side reactions give rise to the formation the metallacycles  $\text{Cp}(\text{CO})_2\text{M}-\text{P}(\text{tBu})(\text{Cl})-\text{PtBu}$  (4) or the dinuclear  $\text{M}=\text{P}$  complex  $\text{Cp}(\text{CO})_2\text{M}=\text{P}(\text{Mes})-\text{M}(\text{CO})_2[\text{P}(\text{Mes})\text{H}_2]\text{Cp}$  (5). Compounds of the type 2 are extremely reactive concerning the exchange of P-bonded hydrogen chlorine atom. In this context H/Cl-exchange with  $\text{CCl}_4$  can be realized as well as the substitution of chlorine against  $\text{RO}^-$ ,  $\text{RS}^-$ ,  $\text{R}_2\text{N}^-$  and the metal anions  $\text{C}_5\text{R}_5(\text{CO})_3\text{M}^-$  ( $\text{R} = \text{H}, \text{Me}$ ). Experiments to convert 2 to  $[\text{Cp}(\text{CO})_2\text{M}=\text{PR}]^+$  have so far been unsuccessful.

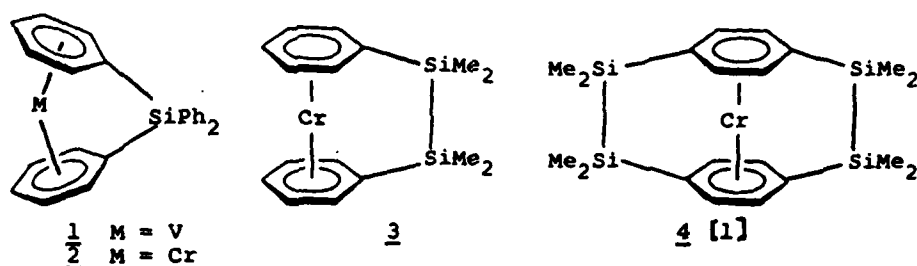
The chiral metal phosphorus double bond complexes  $\text{Cp}(\text{CO})(\text{R}_2\text{PH})\text{M}=\text{PR}_2$  (7) ( $\text{R}_2\text{P} = \text{Ph}_2\text{P}, \text{t-Bu}(\text{Ph})\text{P}$ ) are obtained via dehydrohalogenation of  $\text{Cp}(\text{CO})(\text{R}_2\text{PH})_2\text{MCl}$  (6) with  $\text{Me}_3\text{P}=\text{CH}_2$ . 7 can be further deprotonated to the anionic diphosphetametallo-allyl species  $[\text{Cp}(\text{CO})(\text{R}_2\text{P})_2\text{M}]^-$  (8), which represents an attractive building block in cluster synthesis. The structure, the spectroscopic data and the reactivity of 7, 8 are discussed.

## SILA-METALLOCYCLOPHANES

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Gerhardt Baum

Fachbereich Chemie, Philipps-Universität,  
Hans-Meerwein-Strasse, D-3550 Marburg (FRG)

By means of wet-chemical methods and by metal-atom ligand-vapor cocondensation techniques we have prepared bis( $\eta^6$ -arene) metal complexes containing  $-R_2Si-$  as well as  $-R_4Si_2-$  groups as interannular bridges (sila-metallocyclophanes):



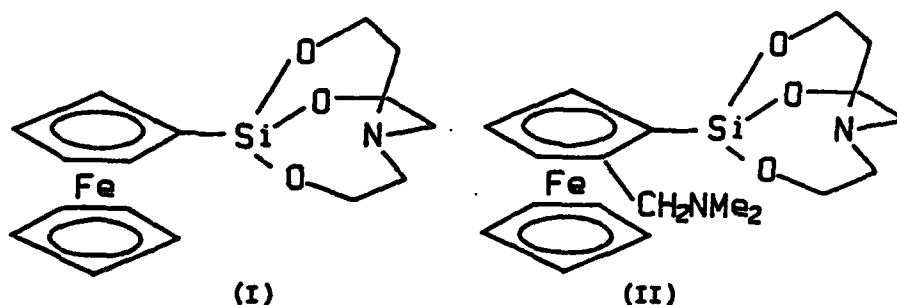
1 and 4 are characterized by X-ray crystallography, the paramagnetic species 1 $\cdot$ , 2 $^+$ , 3 $^+$ , and 4 $^+$  are studied by EPR-spectroscopy. Topics of interest include the effect of ring tilt on metal-ligand spin delocalization, the influence  $\eta^{12}$ -coordination of a transition metal atom exerts on the structure of the parent cyclophane and the prospect of constructing hetero-cyclophanes taking advantage of the template effect. Work towards accomplishing higher degrees of interannular bridging and towards substitution of germanium and tin for silicon in order to fine tune the dimension of the sandwich cavity is in progress and will be reported in due course.

[1] Ch.Elschenbroich, J.Hurley, W.Massa, G.Baum  
Angew.Chem.100(1988) in print

## FERROCENYLSILATRANES

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Silatrane are pentacoordinated silicon compounds of pharmaceutical interest<sup>1)</sup>. Although many derivatives with different substituents at silicon have been reported, no silatrane with metallocene substituents have ever been prepared. The first members of this class of compounds will be presented here.



The silatrane (I) and (II) are prepared in the usual way<sup>2)</sup>, i.e. by transesterification of triethoxysilanes with triethanolamine, or by direct reaction of ethoxysilatrane with lithiated ferrocenes. (I) and (II) show the normal spectroscopic behaviour of ferrocene and silatrane derivatives, and the NMR chemical shifts of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{29}\text{Si}$  lie in the range expected for such compounds. Comparing the silatrane with the corresponding triethoxysilanes, the upfield shift in the  $^{29}\text{Si}$  NMR spectra confirms the widening of the coordination sphere by the formation of the nitrogen-silicon bond. Interestingly, a considerable lowering of the redox potential corresponding to the reversible  $\text{Fe}^{\text{II/III}}$  transition is observed comparing the triethoxysilanes with the silatrane ( $\Delta E_{1/2}^{\text{ox}} = 0.26 \text{ V}$  for (I) and  $0.14 \text{ V}$  for (II)). The redox potentials of the triethoxysilanes are almost the same as the unsubstituted ferrocene, while the much lower potentials of the silatrane suggest a considerable transmission of electron density from nitrogen to iron via silicon. Mechanisms for this transmission will be discussed.

1) M.G.Voronkov, *Top.Curr.Chem.* **84**, 77 (1979).

2) M.G.Voronkov, *Pure Appl.Chem.* **12**, 35 (1966).

SYNTHESIS, STRUCTURE AND REACTIVITY OF THE GERMENE  $\text{Mes}_2\text{Ge}=\text{CR}_2$ 

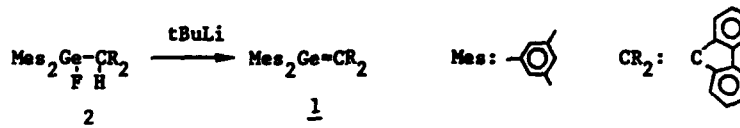
J. Escudie, C. Courat, M. Lazraq, J. Satgé

Laboratoire de Chimie des Organomineaux, UA 477, Université P. Sabatier  
118 route de Narbonne, 31062 Toulouse cedex, France

and M. Dräger

Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg  
Universität, Johann-Joachim-Becher-Weg 24, D-6500 Mainz, Germany

The germene 1, first stable compound with a germanium-carbon double bond<sup>1</sup>, has recently been synthesized by dehydrofluorination of the fluorogermene 2 :



X-ray structure of 1 has been determined<sup>2</sup>: the germanium atom is planar and the germanium-carbon double bond (1.80 Å) is shortened by about 10.5% in relation to the corresponding single bond in the germane  $\text{Mes}_2\text{Ge}(\text{H})\text{C}(\text{H})\text{R}_2$ . Strong mesomeric effects, corroborated by calculations, are observed between the  $\text{Ge}=\text{C}$  double bond and the fluorenylidene group, and also for the first time across the germanium atom.

Reactivity of 1 is very important towards electrophiles (protic reagents, halogens...), nucleophiles (lithio compounds, hydrides...) which add onto the double bond.

Many cycloaddition reactions have been observed : [2+1] (sulfur), [2+2] (azo compounds, imines, aldehydes and ketones), [2+3] (nitrones, diazo compounds) and [2+4] (1,3-dienes,  $\alpha$ -ethylenic aldehydes and ketones) with formation of novel three, four, five and six-membered rings.

The germene 1 appears as a very interesting new synthon in organometallic chemistry.

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W.-W. du Mont, L. Lange, D. Sewing, T. Severengiz, I. Wagner, Fachbereich Chemie  
 Universität Oldenburg, Postfach 25 03, D-2900 Oldenburg, RFA

#### I. GENERATION AND DECOMPOSITION OF C=Te DOUBLE BOND SPECIES

Bis(trimethylsilyl)telluride **1** and di(pivaloyl)telluride **2a** react to give pivaloyl(trimethylsilyl)telluride [trimethylsilyl telluropivaloate] **3a**, which exists in a dynamic equilibrium with the C=Te-bonded isomer **4a**. **3a** and **4a** are related by an intramolecular 1,3-trimethylsilyl shift; (2+4)cycloaddition reactions with the C=Te bond lead to complete consumption of **3** and **4** <sup>[1]</sup>. Sterically less congested **4**, obtained from **1** with diacetyltelluride **2b** (confirmed by mass spectra and trapping experiments) decomposes spontaneously to give E- and Z-bis(trimethylsiloxy)buten (**2**).

#### II. APPROACH TO STERICALLY CONGESTED MOLECULES WITH Ge=S OR Ge=Se BONDS

Bis(2,4,6-tri-tert-butylphenyl)germanium(II), **5**, the first isolated diarylgermylene, rearranges within several hours at room temperature to an isomeric germaindane **6** <sup>[2]</sup>. With sulfur, **5** reacts at low temperature to germaindanthiol **7**. The spontaneous C,H activation at one ortho-tert-butyl group of germathione **6** by an adjacent Ge=S bond deserves interest. Corresponding experiments, that might lead to Ge=Se or Ge=Te bonds, will be reported.

#### III. FORMATION AND STABILISATION OF THE FIRST SELENO GERMYLENE

Di-coordinate divalent germanium species are known with bulky substituents that contain, C, N, O, or S-atoms bonded to germanium. Stable monomeric germynes with less electronegative, and highly polarizable atoms [from the 4th and 5th period] attached to germanium have not yet been isolated. Bis(2,4,6-tri-tert-butylphenyl)seleno)germanium(II) **8** was generated from the corresponding lithium reagent with GeCl<sub>2</sub>-dioxane at -78°C ... -40°C. Isolation of pure **8** at room temperature failed, but pure Dichloro(2,4,6-tri-tert-butylphenyl)seleno)germanium(IV) **9** was obtained in low yield. Trapping of **8** with W(CO)<sub>5</sub>·THF led to yellow crystalline [W(CO)<sub>5</sub>·**8**], the monomeric germylene complex **10**.

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# SYNTHESIS AND CATALYTIC ACTIVITY OF CARBONYL PALLADIUM CLUSTERS

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Palladium compounds are known to catalyze carbonylation reactions of unsaturated hydrocarbons, haloalkyls, carboxylic acids, alcohols, nitroaromatic derivatives [1, 2]. This attracts attention to carbonyl palladium complexes [3, 4].

Synthesis and properties of carbonyl clusters with Pd<sub>4</sub>-core [5, 6] will be considered. The dehydration of alcohols catalyzed by heteronuclear Pd,Mo-cluster Na<sub>2</sub>Pd<sub>4</sub>Mo<sub>4</sub>(CO)<sub>12</sub>Cp<sub>4</sub> [7, 8] under mild conditions will be discussed.

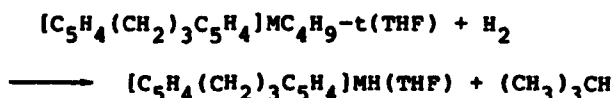
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ORGANO RARE EARTH HYDRIDES WITH  
CHELATING BISCYCLOPENTADIENE LIGAND

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The  $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]\text{MC}_4\text{H}_9\text{-t}(\text{THF})$  complexes react with dihydrogen in toluene under mild conditions to yield a new class of organo rare earth hydrides with a chelating biscyclopentadiene ligand  $[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]\text{MH}(\text{THF})$  ( $\text{M}=\text{Y}, \text{Er}, \text{Lu}$ ). These hydrides have been



characterized by IR, MS,  $^1\text{H}$  NMR spectroscopy and elemental analysis. They are stable enough to be isolated and identified at ambient temperature. The factors which have been presumed to influence the cleavage of M-C bond in precursors and the formation of M-H bond are discussed.

Treatment of the hydrides obtained with 1-hexene in tetrahydrofuran produces hexane in good yield, moreover the hydrides are able to hydrogenate catalytically 1-hexene under mild conditions.

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C-X ACTIVATION WITH  $\text{Cp}_2^*\text{MH}$  AND  $\text{Cp}_2^*\text{MCH}(\text{SiMe}_3)_2$  DERIVATIVES OF Y, La, AND Ce.

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In our study on the reactivity of metallocene hydride and alkyl compounds of Y, La, and Ce we found remarkable selectivity differences for the activation C-X bonds.

Thermolysis of  $\text{Cp}_2^*\text{MCH}(\text{SiMe}_3)_2$  in toluene gave a mixture of products for  $\text{M} = \text{Y}$ , but for  $\text{M} = \text{La}$  and  $\text{Ce}$  exclusive activation of  $\text{sp}^3\text{-C-H}$  bonds with formation of the benzyl derivative (Fig. 1) was observed (eq 1).

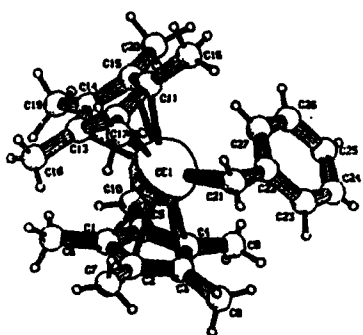
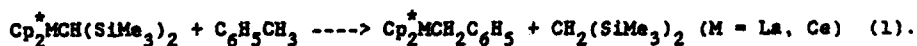


Fig. 1.

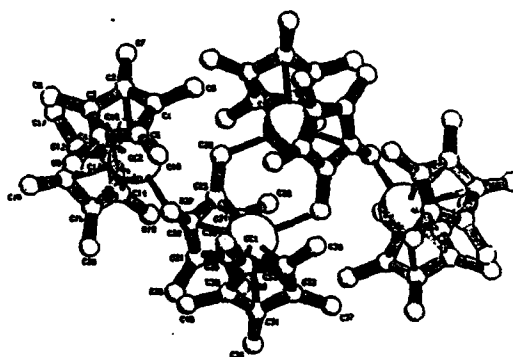
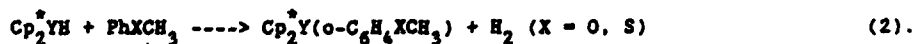


Fig. 2.

Thermolyses in an inert solvent like cyclohexane again showed the formation of  $\text{CH}_2(\text{SiMe}_3)_2$ . For  $\text{M} = \text{Ce}$  selective double hydrogen abstraction from the  $\text{Cp}^*\text{-methyl}$  groups took place (Fig. 2). The intriguing product is a tetramer with bridging  $\text{C}_5\text{Me}_5(\text{CH}_2)_2$ -groups.

For  $\text{Cp}_2^*\text{YH}$  both C-H and C-X activation was observed. Ortho directing groups like  $-\text{OCH}_3$  and  $-\text{SCH}_3$  provide selective C-H activation of ortho C-H bonds (eq 2). In contrast to this, aliphatic ethers show activation of the C-O bond (eq 3).



REACTIVITY AND CATALYTIC PROPERTIES OF NAPHTHALENE  
AND ANTHRACENE COMPLEXES OF YTTERBIUM

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Recently we have found that interaction of the anhydrous lanthanoid halides with naphthalene sodium or naphthalene lithium leads to the formation of high reactive naphthalene complexes of lanthanoids  $C_{10}H_8Ln_x(MHal)_y$  ( $Ln = Sm, Eu, Yb$ ;  $M = Li, Na$ ;  $Hal = Cl, Br, I$ ;  $x = 1-5$ ;  $y = 0-3$ ) [1].

The complex  $C_{10}H_8Yb_2(I)$  shows high catalytic activity in the reactions with oxygencontaining reagents and unsaturated hydrocarbons. The compound I catalyzes polymerization reactions of epoxides, styrene, methyl methacrylate, isoprene and piperilene. It also catalyzes copolymerisation reaction of ethyleneoxide with styrene and isoprene, and reaction of epoxides with  $CO_2$  which leads to alkylencarbonates  $RCH-CH_2-CO_2O$ .

Reaction of I with  $Ph_3GeH$  (THF,  $20^\circ C$ ) gives a metalhydride complex of the new type  $(Ph_3GeH)_2Yb \cdot (THF)_4$ . It was isolated as the yellow diamagnetic crystals, soluble in THF, toluene, m.p.  $129-133^\circ C$  (dec.). X-Ray analysis shows that the molecule of the product is distorted octahedron. The grouping  $GeHYbHGe$  is almost colinear: the  $Ge-H-Yb$  angle is  $169.4$ , and  $168.8^\circ$ , the  $H-Yb-H$  angle is  $179.0^\circ$ , the  $Ge-H$  distances are  $1.61$  and  $1.65 \text{ \AA}$ , the  $Yb-H$  distances are  $1.56$  and  $1.51 \text{ \AA}$ . Molecules of THF lei in equatorial plane. Anthracene complex  $C_{14}H_{10}Yb_2(NaCl)_3$  was obtained as the black pyrophoric insoluble powder by reaction of  $YbCl_3$  with anthracene sodium. It reacts with  $O_2$ ,  $H_2O$ ,  $CO_2$ ,  $C_6H_6$ ,  $(Me_3Si)_2NH$  and  $CH_2CH_2O$  like naphthalene complex but reactions are slower and give lower yields of the corresponding products.

I. M.N.Bochkarev, A.A.Trifonov, V.K.Cherkasov, G.A.Razuvaev,  
Abstr. VIII FECHEN Conf. Organometal Chem., Toledo, (1987),  
p. 152; Zh. Obshch. Khim. 58(1988)719.

**THE PREPARATION OF DIVALENT AMIDO-LANTHANIDS BY PROTOLYTIC CLEAVAGE OF  $(C_6F_5)_2M$  ( $M = Sm, Eu, Yb$ ) - EVIDENCE FOR THE FORMATION OF  $(C_6F_5)_2Sm$  FROM  $(C_6F_5)_2Hg$  AND METALLIC SAMARIUM.**

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The bis(pentafluorophenyl)lanthanoid complexes,  $(C_6F_5)_2M$  ( $M = Eu, Yb$ ), which are readily prepared by transmetallation of  $(C_6F_5)_2Hg$  with europium or ytterbium, (eq.(1)), react with weak N-acids, displacing pentafluorobenzene and forming divalent amido-lanthanoids (eq.(2)).

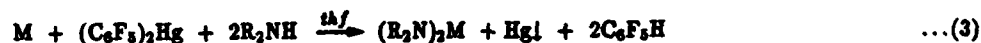


$M = Eu, Yb$ .



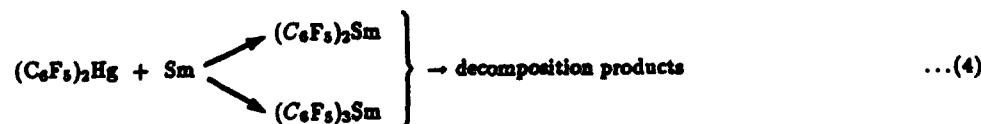
$R_2NH = \text{carbazole, 2-phenylindole}$

Prior formation of the  $(C_6F_5)_2M$  reagent can be omitted by using a "one-pot" synthesis, viz - direct reaction of the metal,  $(C_6F_5)_2Hg$  and the amine (eq.(3)).



$M = Eu, Yb; R_2NH = 2\text{-phenylindole}$

The reaction of  $(C_6F_5)_2Hg$  with samarium metal, in contrast with that for europium and ytterbium, yields a variety of products which are considered to be derived from decomposition of initially formed  $(C_6F_5)_2Sm$  and/or  $(C_6F_5)_3Sm$  species (eq.(4)).

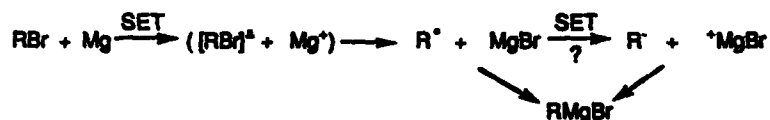


However, by utilising the "one-pot" reaction (eq.(3)  $M = Sm$ ) the thf soluble, divalent amido-samarium complex,  $(2\text{-phenylindol-1-yl})_2Sm(thf)_4$  was prepared. This provides substantial evidence for the formation of  $(C_6F_5)_2Sm$  from the transmetallation reaction.

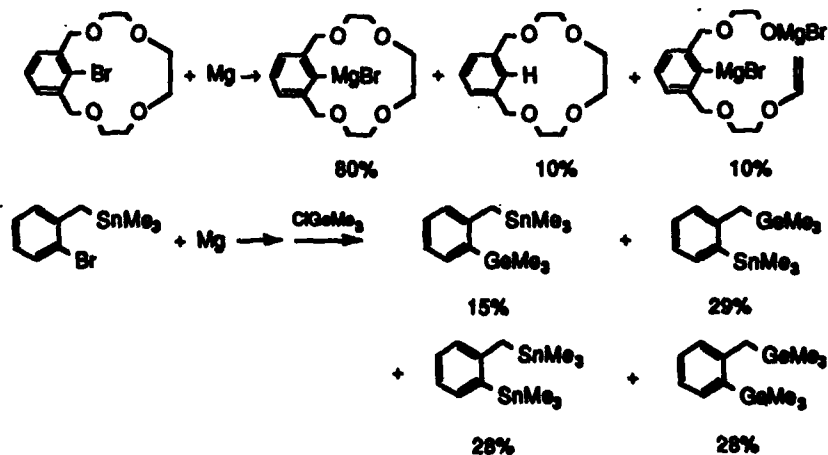
## CARBANIONOID INTERMEDIATES IN THE GRIGNARD FORMATION REACTION

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The famous and preparatively important formation of Grignard reagents from organic halides has been the subject of intensive mechanistic investigation. Although the heterogeneous character of the reaction and the (extremely) short half life of the many intermediates posed major obstacles, the following scheme has gradually emerged, and there is widespread agreement on most of its features.



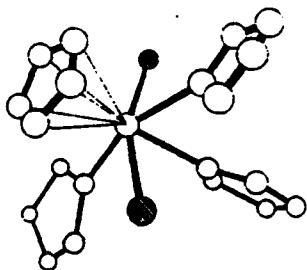
Uncertainty exists amongst others on the latter stages of the reaction. Thus, there is no doubt that the radical R and MgBr combine to give RMgBr, but it is mostly assumed that this combination is a direct one without the intermediate formation by a single electron transfer (SET) of the (more or less free) carbanion R<sup>-</sup>. We present evidence from two completely unrelated systems exhibiting two completely different, but highly diagnostic modes of reactivity, which point to R<sup>-</sup> as a true intermediate:



MONOCYCLOPENTADIENYL LANTHANIDE(III) COMPLEXES. I. THE CRYSTAL AND  
MOLECULAR STRUCTURE OF THE mer,trans EUROPIUM(III) COMPLEX  
 $(\eta^5\text{-C}_5\text{H}_5)\text{EuCl}_2(\text{THF})_3$

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Marzolo, 1, 35141- Padova - Italy

As a part of a spectroscopic study on europium(II and III)  
organometallic derivatives, the solid state structure of the  
compound obtained by reacting (1)  $\text{NaC}_5\text{H}_5$  and  $\text{EuCl}_3$  in  
tetrahydrofuran (molar ratio=1) is reported. Structural data on  
monocyclopentadienyl complexes of the type  $(\text{C}_5\text{H}_5)\text{LnCl}_2(\text{THF})_3$   
(Ln=Lanthanide; THF = tetrahydrofuran) are known only for  
Ln=Er(2). Since the size of the lanthanide metal seems to have "a  
pronounced influence on the structural makeup of Cp-compounds",  
(1) we have investigated possible conformational changes in the  
solid state, in the "gadolinium break" region of the lanthanide  
series. The title compound shows in the solid state the same ar-  
rangement of the ligands found in the erbium(III) analogue.



Crystal data. The purple single crystals  
of  $(\eta^5\text{-C}_5\text{H}_5)\text{EuCl}_2(\text{THF})_3$  are monoclinic,  
space group  $\text{P}2_1/\text{n}$  with four molecules  
in a unit cell of  
dimensions:  $a=15.258(3)$ ,  $b=17.216(3)$ ,  
 $c=7.860(1)\text{\AA}$ ,  $\beta=95.5(3)^\circ$ .

The europium(III) ion is coordinated by  
two chloride two chloride ions, three  
tetrahydrofuran oxygen atoms and the  
cyclopentadienyl group bonded in a  
penta- hapto fashion. (see Figure).

The europium(III) coordination sphere can be described as  
distorted octahedral with the  $\eta^5\text{-C}_5\text{H}_5$  ligand formally occupying  
one of the polyhedral vertices. The THF molecules have a  
meridional disposition and the chlorine atoms occupy  
approximately trans sites.

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# ELECTRON RICH METAL COMPLEXES FOR CO<sub>2</sub> AND CS<sub>2</sub> INCORPORATION

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The synthesis of some new dinitrogen and ethylene complexes of Mo and W has been carried out and their reactivity towards CO<sub>2</sub> and CS<sub>2</sub> has been studied. While CO<sub>2</sub> reacts with the compounds trans-M(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>, (M= Mo, W), with formation of the white acrylate complexes [M(CH<sub>2</sub>=CHCO<sub>2</sub>)H(C<sub>2</sub>H<sub>4</sub>)(PMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, the reaction with CS<sub>2</sub> affords an almost black material of composition M(CS<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(PMe<sub>3</sub>)<sub>3</sub>, which has been shown to contain an η<sup>3</sup>-C<sub>2</sub>S<sub>4</sub> fragment, resulting from the reductive head-to-tail coupling of two molecules of CS<sub>2</sub>. CO symmetrically cleaves the C<sub>2</sub>S<sub>4</sub> group of this complex and yields the M(O) species Mo(S<sub>2</sub>CPMe<sub>3</sub>)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>.

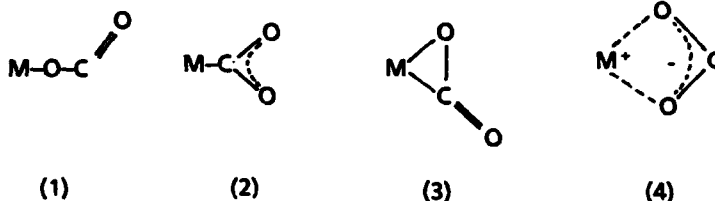
The reactivity of some nickelacyclopentene complexes, L<sub>2</sub>Ni(CH<sub>2</sub>CMe<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>), towards CO<sub>2</sub> and CS<sub>2</sub>, has also been investigated. While anhydrous CO<sub>2</sub> produces only the nickelalactone complex (PMe<sub>3</sub>)<sub>2</sub>Ni(CH<sub>2</sub>CMe<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>), excess of CS<sub>2</sub> reacts with formation of Ni(C<sub>2</sub>S<sub>4</sub>PMe<sub>3</sub>)(PMe<sub>3</sub>), (J.A. Ibers, 1982), and the thiolactone S=C(S)CH<sub>2</sub>CMe<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>. A possible pathway for this reaction has been established by the isolation of the intermediate η<sup>2</sup>-C,S dithiolactone complex (PMe<sub>3</sub>)<sub>2</sub>Ni(S=C(S)CH<sub>2</sub>C(Me)<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>). The dmpe derivative, (dmpe)Ni(CH<sub>2</sub>C(Me)<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>) reacts with excess CS<sub>2</sub> with formation of the trithiocarbonate (dmpe)Ni(CS<sub>3</sub>) and of the tioketone S=CCH<sub>2</sub>C(Me)<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>. This process can formally be regarded as a reductive disproportionation of CS<sub>2</sub> although it takes place without change in the oxydation state of the metal. The reaction seems to imply an insertion of CS<sub>2</sub> as the first step, and this has been confirmed by isolation of the dithiolate complex (dmpe)Ni(S<sub>2</sub>CCH<sub>2</sub>CMe<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>).



# VIBRATIONAL SPECTROSCOPIC STUDIES OF SOME CARBON DIOXIDE COMPLEXES

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Some transition metal atoms in low valency state form complexes with CO<sub>2</sub>, leading to the following structures :



A systematic study of the reactivity of CO<sub>2</sub> toward transition metal atoms at zero oxidation state has been realized in low temperature matrices by means of F.T.I.R. spectroscopy in an attempt to learn more about the binding of CO<sub>2</sub> with transition metal atoms. Structures (1) (2) (3) have been observed, depending on the nature of the metal and the matrix, leading to different reactivities upon annealing or irradiation.

IR bands alone do not allow to discriminate between the different structures but the situation is more favorable if we look at the isotopic shifts of the stretching and bending modes of coordinated CO<sub>2</sub>, using <sup>13</sup>CO<sub>2</sub> and C<sup>18</sup>O<sub>2</sub>.

So structural conclusions and schematic pathways of reactions can be based on the isotopic shifts observed in IR spectra and normal coordinate calculations have been carried out for structures (1) (2) and (3). Compared with the free molecule, the force constants of coordinated CO<sub>2</sub> are significantly decreased (-50 %) and OCO angle is typically between 120 and 150°.

To improve our analysis, we also calculate force constants for some structurally already known complexes and transfer them to our models : e.g., the valence force field of (PCy<sub>3</sub>)<sub>2</sub>Ni(CO<sub>2</sub>) (a) and (PMe<sub>3</sub>)<sub>4</sub>Mo(CO<sub>2</sub>)<sub>2</sub> (b) are determined from the IR and Raman frequencies of complexes and some labeled derivatives.

(a) collaboration with M.ARESTA, Univ.Bari, Italy

(b) collaboration with E.CARMONA, Univ. Sevilla, Spain.

A HETEROBIMETALLIC APPROACH TO  
C/O BOND SCISSION OF CO<sub>2</sub>.

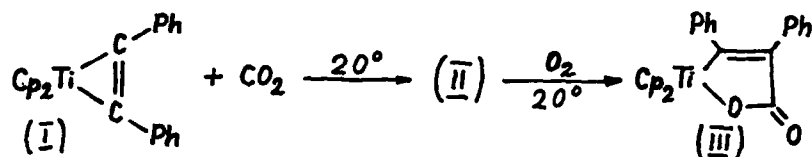
E. G. Lundquist, J. C. Huffman, and Kenneth G. Caulton,  
Department of Chemistry and Molecular Structure Center,  
Bloomington, IN 47405 (U.S.A.).

The heterobimetallic polyhydride (COD)RhH<sub>3</sub>OsP<sub>3</sub> (COD  $\equiv$  1,5-cyclooctadiene; P  $\equiv$  PMe<sub>2</sub>Ph) reacts with CO<sub>2</sub> at 1 atm and 25° to produce H<sub>2</sub>Os(CO)P<sub>3</sub>, (COD)<sub>2</sub>Rh<sub>2</sub>P<sub>3</sub>OsH<sub>2</sub>CO<sub>2</sub> and H<sub>2</sub>O. Hydride transfer thus effects reduction of CO<sub>2</sub> to CO. The Rh<sub>2</sub>Os cluster has been shown by spectroscopic studies and X-ray diffraction to contain CO<sub>2</sub> in a highly bent geometry, this ligand being coplanar with and bonded to all three metals. Attempts to probe the reactivity of this tightly-bound CO<sub>2</sub> moiety reveal it to be subject to electrophilic attack, detected initially by changes in <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR parameters. The bonding in the resulting adducts has been established in one example, by X-ray diffraction of the product from Zn<sup>2+</sup>.

# INTERACTION OF A TOLANE COMPLEX OF TITANOCENE WITH CARBON DIOXIDE

Vladimir Burlakov, Alexander Yanovsky, Yuri Struchkov, Vladimir Shur and Mark Vol'pin, Institute of Organo-Element Compounds of the USSR Academy of Sciences, Vavilov St. 28, Moscow 117813, USSR

We have found that a complex of titanocene with tolane  $\text{Cp}_2\text{Ti}(\text{C}_2\text{Ph}_2)$  (I) [1] readily reacts with carbon dioxide at room temperature and atmospheric pressure. On carrying out the reaction in hexane the product (II) is formed, a subsequent interaction of which with the air oxygen results in rapid formation of titanadihydrofuranone metallacycle (III). The structure of the complex III has been proved by an X-ray analysis ( $\lambda\text{Mo}$ , 2713 reflections,  $R=0.031$ ); the structure of II is under investigation and the results of this study will be presented.



Complex III is an air-stable, red, crystalline substance (m.p. 261-262°C(dec.) under Ar) soluble in  $\text{CH}_2\text{Cl}_2$  and poorly soluble in ethers and hydrocarbons. The titanadihydrofuranone cycle  $\text{TiOC}_3$  in III has an envelope conformation. The Ti atom is displaced from the  $\text{OC}_3$  plane by 0.222(1) Å, the  $\text{TiOC}/\text{OC}_3$  dihedral angle is equal to 7.9(2)°. Geometry of coordination environment of the Ti atom is unexceptional. The Cp ring planes in the wedge-like sandwich form the dihedral angle of 133.4(1)°, the Ti-C and Ti-O bond lengths in the metallacycle are equal to 2.199(1) and 1.964(1) Å respectively.

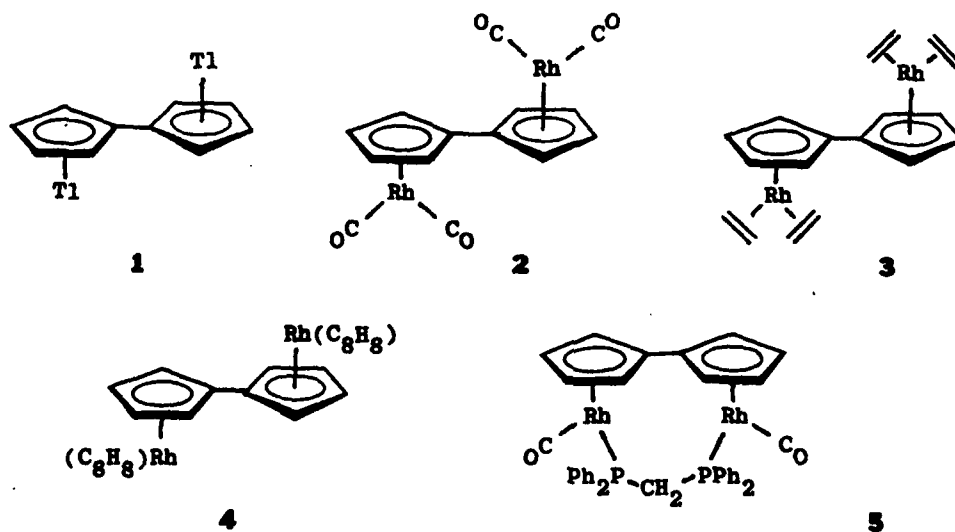
1. V.B.Shur, V.V.Burlakov, M.E.Vol'pin, J.Organomet. Chem., 1988, in press.

## STUDIES ON FULVALENE DERIVATIVES OF GROUP 7 AND 9 METALS

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T. E. Bitterwolf, Department of Chemistry, United States Naval Academy, Annapolis, Maryland 21402 (U.S.A.)

The reaction of thallous ethoxide with halide-free solutions of dihydrofulvalene has produced (fulvalene)dithallium (1) in 85-100% yield. Compound 1 is a brown air-sensitive solid that can be stored at  $-20^{\circ}\text{C}$  for several months. Reactions of 1 with carbonyl halides of manganese, rhenium, cobalt, rhodium and iridium produced the corresponding homobimetallic fulvalene-metal carbonyls in yields of 52-94%. The dirhodium analog (2) reacted with trimethylamine-N-oxide to form a tricarbonyl complex that contained a bridging carbonyl group and a rhodium-rhodium bond. Tetraethylene(fulvalene)-dirhodium (3) and bis(cyclooctatetraene)dirhodium (4) as well as the corresponding bis(1,5-cyclooctadiene) analog have been prepared in excellent yields by reactions of 1 with the corresponding diolefin(chloro)rhodium dimer. Variable temperature proton NMR studies on 3 indicate that the ethylene ligands are fluxional. Photolysis of 4 with  $\text{CpRh}(\text{C}_2\text{H}_4)_2$  in THF solution has produced a novel tetranuclear rhodium complex in 27% yield. Reaction of 2 with  $(\text{Ph}_2\text{P})_2\text{CH}_2$  has led to a bridged derivative (5) that has been the subject of chemical oxidation and protonation studies. The structures of 2 and 3 have been confirmed by X-ray diffraction analyses.

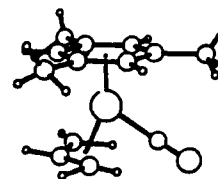


## A STUDY OF HALF-SANDWICH ARENE-IRON (II) COMPLEXES

Anthony H. Wright and Shaker Puntambekar, Chemistry Department,  
University of Nottingham, Nottingham, NG7 2RD, U.K.

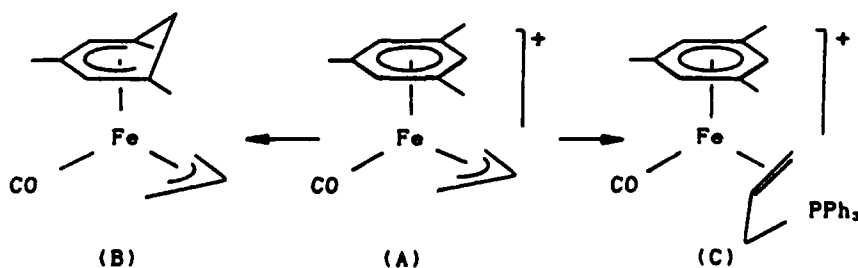
One of the major branches of organoiron chemistry is based on half sandwich chemistry, based on complexes such as  $\text{CpFeXL}_2$ . The comparable chemistry for arene-iron complexes is minimal. This is because their appropriate synthetic routes to half-sandwich iron (II) complexes have not been available.

A new method for making both sandwich and half-sandwich arene-iron complexes will be outlined. The products, such as  $[(\text{C}_6\text{H}_5\text{Me})\text{Fe}(\text{C}_3\text{H}_5)(\text{CO})]\text{PF}_6$  (A) are air stable but highly reactive fulfilling the anticipation of a rich chemistry. As might be expected for these electron-rich species, the neutral derivatives are however air sensitive.



(A)

Preliminary investigations of reactivity indicate that both metal-based and arene-based reactions are common. Results including arene substitution, and nucleophilic addition will be described.



(B)

(A)

(C)

The site of nucleophilic substitution is critically dependant on the nature of the nucleophile. Thus simple hydride addition gives the predicted Green-Mingos product (B), but phosphines add to the allyl ligand (C).

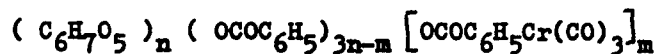
THE INCLUSION AND COVALENT ORGANOMETALLIC DERIVATIVES  
OF CYCLODEXTRINS

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Organo-Element Compounds, Vavilov St., 28, 117813 Moscow, U.S.S.R.

The cyclodextrin complexes with organometallic derivatives of iron, ruthenium, osmium, rhodium and some other transition metals have been prepared in solid state from aqueous solution. They are used to carry hydrophobic  $\pi$ -cyclopentadienyl or  $\pi$ -arene ligands.

Induced Cotton effects in the circular dichroism spectra which correspond to the chromophores of the molecules included have been investigated, as well as equilibrium constants for some ferrocenes have been determined in the ethylene glycol solution.

Several modified  $\alpha$ - and  $\beta$ -cyclodextrins having  $\sigma$ -bonded ferrocenyl or arylchromiumtricarbonyl groups have been synthesized such as  $\pi$ -complexed per-benzoyl derivatives



$$n = 7, \quad m = 2;$$

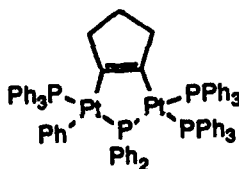
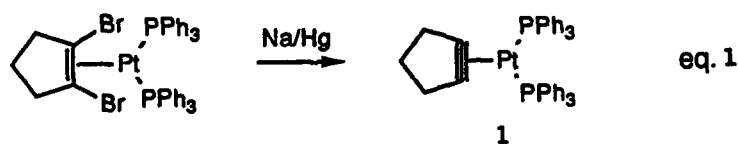
$$n = 6, \quad m = 1$$

# THE STABILIZATION AND REACTIVITY OF HIGHLY STRAINED CYCLIC ALKYNES ON TRANSITION METAL CENTRES

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The smallest carbocyclic acetylene that can be isolated in the free state is the eight-membered ring cyclooctyne. Smaller cycloalkynes and benzyne (didehydrobenzene) are transient molecules that can be stabilized by formation of mononuclear metal complexes, especially with the  $d^{10}$  elements nickel(0) and platinum(0).

This lecture will describe the synthesis and reactivity of a series of  $\eta^2$ -benzyne complexes  $M(\eta^2-C_6H_4)L_2$  ( $M = Ni, Pt$ ;  $L_2 =$  various monodentate and bidentate tertiary phosphines)<sup>1</sup>, together with the formation of a dinuclear nickel(0) complex of 1,4-benzdiyne (1,2,4,5-tetradehydrobenzene),  $\mu$ -1,4- $C_6H_2Ni_2(Cy_2PCH_2CH_2PCy_2)_2$ . The generation of the first metal complex of cyclopentyne, (1), will be reported (eq 1). This molecule is clearly more strained than its long-known cyclohexyne analogue<sup>2</sup>; in the presence of polar solvents, one of its  $PPh_3$  ligands undergoes spontaneous P-Ph bond cleavage to give the dimer 2.



1. M.A. Bennett, T.W. Hambley, N.K. Roberts and G.B. Robertson, *Organometallics*, 4(1985)1992.
2. M.A. Bennett and T. Yoshida, *J. Amer. Chem. Soc.* 100(1978)1750.

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF MANGANESE AND  
CHROMIUM ACETYLENE COMPLEXES

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Laboratorium für Anorganische Chemie der Universität Bayreuth,  
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The acetylene complexes  $\text{Cp}'(\text{CO})_2\text{MnC}_2\text{H}_2$  (**1**) ( $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$ ,  $\eta^5\text{-C}_5\text{H}_4\text{Me}$ ,  $\eta^5\text{-C}_5\text{Me}_5$ ) and  $\text{Ar}(\text{CO})_2\text{CrC}_2\text{H}_2$  (**2**) ( $\text{Ar} = \eta^6\text{-C}_6\text{H}_6$ ,  $\eta^6\text{-C}_6\text{H}_3\text{Me}_3$ ,  $\eta^6\text{-C}_6\text{Me}_6$ ) can be prepared by the photo-induced reaction of the corresponding tricarbonyl compounds and acetylene. Complexes **1** and **2** react with various phosphines, amines, alcohols and hydrazines yielding ylidic carbene-, ylidic vinylidene-, aminocarbene-, carbene- and acetonitrile complexes. The various products were characterized by IR and NMR spectroscopy as well as X-ray structures in some cases.



Isocyanides, good ligands for the stabilisation of tungsten carbyne complexes in low and high oxidation states

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Carbyne complexes of the general type  $\text{I}(\text{CO})_2\text{L}_2\text{W}\equiv\text{CNet}_2$  (I:  $\text{L}=\text{py}$ , II:  $\text{L}_2=2.2'$ -bipy, III:  $\text{L}_2=\text{ophen}$ ) /1/ are easily accessible, useful starting materials for the preparation of neutral and cationic isocyanide substituted carbyne complexes of tungsten in low and high oxidation states. Thus the pyridine ligands in I can be readily replaced by RNC to yield  $\text{I}(\text{CO})_2(\text{RNC})_2\text{W}\equiv\text{CNet}_2$  (IV:  $\text{R}=\text{Me}$ , V:  $\text{R}=\text{t-C}_4\text{H}_9$ ). Upon oxidative decarbonylation with iodine, IV and V are transformed to the seven coordinated complexes  $(\text{I})_3(\text{CO})(\text{RNC})_2\text{W}\equiv\text{CNet}_2$ , which react with excess RNC upon elimination of CO to give the cationic compounds  $[(\text{I})_2(\text{RNC})_4\text{W}\equiv\text{CNet}_2]^+ \text{I}^-$  /2/. Following a similar synthetic route, II and III are first oxidized to  $(\text{I})_3(\text{CO})\text{L}_2\text{W}\equiv\text{CNet}_2$  ( $\text{L}_2=2.2'$ -bipy, ophen) and then converted to the cationic species  $[(\text{I})_2(+\text{NC})_2\text{L}_2\text{W}\equiv\text{CNet}_2]^+ \text{I}^-$  ( $\text{L}_2=2.2'$ -bipy, ophen) /3/.

A rich coordination chemistry is observed when  $\text{I}(\text{CO})_2(+\text{NC})_2\text{W}\equiv\text{CNet}_2$  (V) is heated with  $+\text{NC}$ . It loses CO ligands successively to yield  $\text{I}(\text{CO})(+\text{NC})_3\text{W}\equiv\text{CNet}_2$  (VI) and  $\text{I}(+\text{NC})_4\text{W}\equiv\text{CNet}_2$  (VII). In the presence of  $+\text{NC}$ , thermodynamic equilibria between VI or VII and their cationic counterparts  $[(+\text{NC})_4(\text{CO})\text{W}\equiv\text{CNet}_2]^+ \text{I}^-$  (VIII) or  $[(+\text{NC})_5\text{W}\equiv\text{CNet}_2]^+ \text{I}^-$  (IX) exist. These equilibria are dependant on the temperature and the nature of the solvent, and permit the quantitative interconversion of VI and VIII, or VII and IX /4/.

- /1/ A.C.Filippou, E.O.Fischer und J.Okuda, J.Organomet.Chem., 339 (1988) 309.
- /2/ A.C.Filippou, E.O.Fischer und R.Paciello, J.Organomet.Chem., to be published.
- /3/ A.C.Filippou, E.O.Fischer und H.G.Alt, Z.Naturforsch.B, to be published.
- /4/ A.C.Filippou und E.O.Fischer, J.Organomet.Chem., to be published.

REACTIONS OF THE HYDRIDO COMPLEXES  $[\text{Ru}(\text{CO})\text{ClH}(\text{py})(\text{PPh}_3)_2]$  AND  $[\text{Ru}(\text{CO})\text{HL}_2(\text{PPh}_3)_2]$   $\text{ClO}_4$  (L = MeCN, py) WITH ACETYLENES.

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Pedro Noheda, Instituto de Química Orgánica General, C.S.I.C., Juan de la Cierva 3, 28006 Madrid.

Recently we have reported on the reactions of  $[\text{Ru}(\text{CO})\text{ClH}(\text{Me}_2\text{Hpz})(\text{PPh}_3)_2]$  ( $\text{Me}_2\text{Hpz}$  = 3,5-dimethyl-pyrazole) with acetylenes, which were strongly dependent on the solvent nature [1,2].

The reactions of the analogous neutral complex  $[\text{Ru}(\text{CO})\text{ClH}(\text{py})(\text{PPh}_3)_2]$  with terminal acetylenes  $\text{RC}\equiv\text{CH}$  ( $\text{R} = \text{CMe}_3, \text{Ph}, \text{COOMe}, \text{COOEt}$ ) give rise to the expected  $\pi$ -alkenyl complexes derived from a cis-insertion of the alkyne into the Ru-H bond. However the reactions in MeOH yield alkynyl complexes  $[\text{Ru}(\text{CO})(\text{C}\equiv\text{CR})(\text{py})(\text{PPh}_3)_2]$ . These last reactions in the presence of  $\text{NH}_4\text{PF}_6$  give rise to the same alkynyl complexes in the case of  $\text{R} = \text{CMe}_3$  and Ph, but in the reactions with the activated acetylenes ( $\text{R} = \text{COOMe}, \text{COOEt}$ ) not yet well characterized carbene or vinylidene complexes seem to be formed, as in the corresponding reactions of the pyrazole complex.

$[\text{Ru}(\text{CO})\text{H}(\text{py})_2(\text{PPh}_3)_2]\text{ClO}_4$  shows a strong tendency to give catalytic cyclo-trimerization reactions of the alkynes. Only in some cases the expected monoinsertion derivatives could be isolated from the reactions in a molar ratio 1:1 - in  $\text{CH}_2\text{Cl}_2$ . However  $[\text{Ru}(\text{CO})\text{H}(\text{MeCN})_2(\text{PPh}_3)_2]\text{ClO}_4$  yields well characterized monoinsertion derivatives in the same conditions, in which both nitrile ligands are mutually trans, although these ligands were mutually cis in the starting complex.

In the case of the cationic complexes the reactions with dimethyl acetylene dicarboxylate were also studied.

1. A. Romero, A. Santos and A. Vegas, *Organometallics*, 1987, 6, 1584-1586.
2. A. Romero, A. Santos and A. Vegas, *Organometallics* (in press).

**SYNTHESIS AND REACTIVITY OF BIS(PYRAZOL-1-YL)BORATE ALKYLIDYNE  
COMPLEXES OF TUNGSTEN AND MOLYBDENUM**

Anthony F. Hill and F. Gordon A. Stone

Department of Inorganic Chemistry, University of Bristol,  
Bristol BS8 1TS, Great Britain.

The complexes  $[W(=CR)(CO)_2(NC_5H_4Me-4)_2Br]$  (  $R = CH_3$ ,  $C_6H_4Me-4$ ,  $C_6H_3Me_2-2,6$  ) and  $[Mo(=CC_6H_4Me-4)(CO)_2(NC_5H_4Me-4)_2(CF_3CO_2)]$  react with  $K[H_2B(pz)_2]$  (  $pz = \text{pyrazol-1-yl}$  ) in dichloromethane to afford the compounds  $[M(=CR)(CO)_2(NC_5H_4Me-4)(\eta^2-H_2B(pz)_2)]$  (  $M = W$ ,  $R = CH_3$  1a,  $C_6H_4Me-4$  1b,  $C_6H_3Me_2-2,6$  1c;  $M = Mo$ ,  $R = C_6H_4Me-4$  1d ) in high yield.

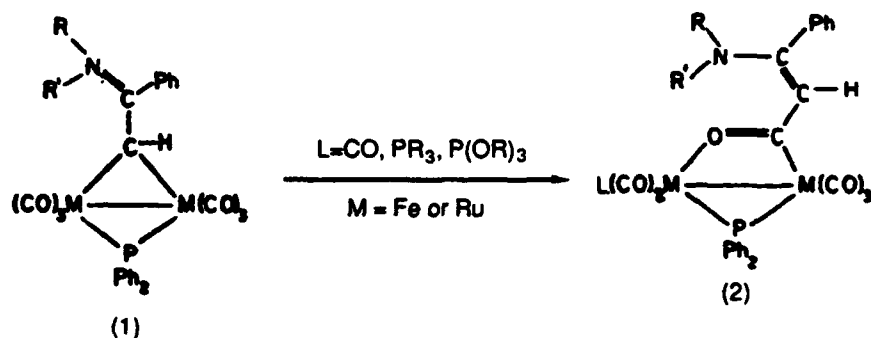
Alternatively, phosphite substituted molybdenum-alkylidyne complexes are accessible from the reaction of  $[Mo(=CC_6H_4OMe-2)(CO)(P(OMe)_3)_3Cl]$  with the salts  $K[H_2B(pz)_2]$  or  $K[Ph_2B(pz)_2]$  giving the compounds  $[Mo(=CC_6H_4OMe-2)(CO)(P(OMe)_3)_2(\eta^2-R_2B(pz)_2)]$  (  $R = H$  2a,  $Ph$  2b )

The compounds 1 and 2 feature coordination of a labile ligand (  $\gamma$ -picoline or phosphite ) cis to the alkylidyne group and this property is seen to dominate the subsequent chemistry.

The reactions of 1 and 2 with phosphines, isonitriles, alkynes, nitrosarenes and chalcogens will be discussed, with particular reference to the rôle of the poly(pyrazol-1-yl) ligand.

Binuclear  $\mu$ -Acyl Complexes via Carbonyl Insertion into a  $\mu$ -Alkylidene Ligand. Graeme Hogarth, Nicholas J. Taylor and Arthur J. Carty, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

The unusual three electron donor  $\mu$ -alkylidene complexes  $[M_2(CO)_6(\mu-PPh_2)(\mu-CHC(Ph)NRR')]$  (1) smoothly insert carbon monoxide in the presence of donor ligands to give the corresponding  $\mu$ -acyl complexes  $[M_2(CO)_5L(\mu-PPh_2)(\mu-O=CCHC(Ph)NRR')]$  (2) in high yield.



U.v. kinetic studies have been performed and show a first order dependence in both starting complex and incoming ligand as well as an interesting solvent dependence. Site selectivity of the incoming ligand is also noted allowing a mechanism for this process to be proposed. Reactivity studies on the  $\mu$ -acyl complexes (2) will be presented.

AQUEOUS AND NON-AQUEOUS CHEMISTRY OF LATE  
TRANSITION METAL  $\sigma$ -ALKYNYL COMPLEXES

Pauline Chow, David Zargarian, Ian R. Jobe, Ian D. Williams,  
Nicholas J. Taylor and Todd B. Marder, The Guelph-Waterloo Centre  
for Graduate Work in Chemistry, University of Waterloo, Waterloo,  
Ontario, N2L 3G1 Canada.

During the course of our studies of the Rh catalyzed cyclization of alkynoic acids to enol lactones, we found<sup>\*</sup> that the complex  $[\text{Rh}(\text{PMe}_3)_4]\text{Cl}$  reacts with terminal alkynes via C-H oxidative addition yielding cis-hydrido- $\sigma$ -alkynyl complexes  $[\text{Rh}(\text{PMe}_3)_4(\text{H})(\text{C}\equiv\text{CR})]\text{Cl}$  (1) in quantitative yield. The reaction can be performed in THF suspension, in which the products are insoluble, or in  $\text{H}_2\text{O}$  wherein the products are very soluble. Similar chemistry has been developed for  $[\text{Rh}(\text{dmpe})_2]\text{Cl}$ , however these cis-hydrido- $\sigma$ -alkynyl complexes slowly isomerize to their trans isomers. Compounds of type (1) can be deprotonated with  $\text{KOH}/\text{H}_2\text{O}$  yielding neutral Rh(I) species  $[\text{Rh}(\text{PMe}_3)_4\text{C}\equiv\text{CR}]$  (2). Analogous  $[\text{Rh}(\text{dmpe})_2\text{C}\equiv\text{CR}]$  complexes have also been prepared. Reactivity patterns of the above complexes along with crystallographic characterization of several classes of Rh  $\sigma$ -alkynyl species will be addressed.

<sup>\*</sup> T.B. Marder, D. Zargarian, J.C. Calabrese, T. Herskovitz and D. Milstein, J. Chem. Soc., Chem. Commun., 1484 (1987).

NEW RESULTS IN ORGANO-f-ELEMENT REACTIVITY,  
THERMOCHEMISTRY, AND CATALYSIS

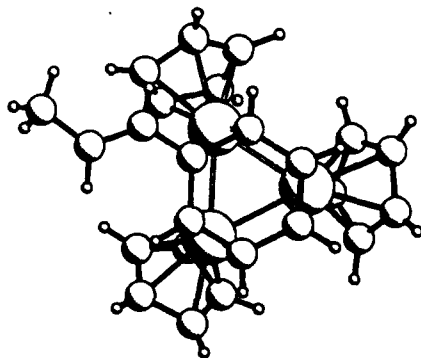
Tobin J. Marks, Department of Chemistry, Northwestern  
University, Evanston, IL 60208, U.S.A.

It is becoming increasingly apparent that metal-ligand bond enthalpy data can afford invaluable insights into important reaction patterns in organometallic chemistry and homogeneous catalysis. Moreover, trends in metal-ligand bonding can be discerned, and unexplored modes of reactivity are sometimes suggested. In this lecture, new results on both relative and absolute metal-ligand bond enthalpies are presented for organoactinides, organolanthanides, and related group 4 organometallic complexes. Striking and chemically significant variations in parameters are noted across the transition series. These can be understood in terms of relatively straightforward bonding concepts, and provide instructive insight into a wide range of  $H_2$ , C-H, C-C, C=C,  $C\equiv C$ , N-H, O-H, and related activation processes. The influence of ancillary ligation on metal-ligand bond enthalpies is also discussed--sometimes it is surprisingly small.

NOVEL TRICOBALT CLUSTERS WITH FACE-CAPPING  
VINYLBENZENE LIGANDS

Hubert Wadepohl, Klaus Büchner and Hans Pritzkow, Anorganisch-  
Chemisches Institut der Universität, Im Neuenheimer Feld 270,  
D-6900 Heidelberg, FRG

Convenient one-pot high-yield syntheses of a variety of novel  $(\text{CpCo})_3(\mu_3-\eta^2:\eta^2:\eta^2\text{-subst.-vinylbenzene})$  clusters are presented. The crystal structure of  $(\text{CpCo})_3(\mu_3-\eta^2:\eta^2:\eta^2\text{-trans-}\omega\text{-methylstyrene})$  reveals a planar arene ligand with nearly equal carbon-carbon bond lengths. In solution mutual rotation of the  $\text{Co}_3$  and arene rings is observed. The bonding in these clusters in relation to chemisorbed arenes on metal surfaces will be discussed.



Preliminary reactivity studies reveal the extraordinary stability of the  $\mu_3$ -arene clusters. Arene exchange is not accomplished without disrupting the metal backbone.

## NEW GERMANIUM - COBALT AND IRON CARBONYL CLUSTERS

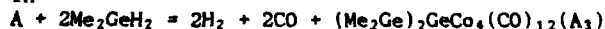
Skelte Anema, Siew Kim Lee, Kenneth M. Mackay, Brian K. Nicholson, and Miranda Service. School of Science, University of Waikato, P.B. Hamilton, New Zealand

In earlier work we have used germanium hydrides to synthesise open clusters containing linked  $\text{GeM}_2$  ( $\text{M}=\text{Co}, \text{Fe}$ ) triangles, such as  $\text{GeCo}_4(\text{CO})_{14}$  (A) (1). Closed clusters, like the pseudo-octahedral  $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$  (B) form by condensation from the open precursors (2), and have been prepared by other routes (3).

We now report:-

(a) a new Ge/Fe homologue of A, namely  $\text{Ge}_2\text{Fe}_4(\text{CO})_{21}$  ( $\text{A}_1$ ), and a related  $\text{Ge}_2\text{Fe}_7(\text{CO})_{26}$  ( $\text{A}_2$ )

(b) that the open networks may be extended by reaction of alkylgermanes as in



(c) the R groups may be varied in molecules of type B, giving mixed substituents such as  $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Co}(\text{CO})_4$  ( $\text{B}_1$ )

(d) the synthesis of a new structural type which may be viewed as a fusion of the A and B structures by sharing a common Co-Co edge,  $[(\text{EtGe})_2\text{Co}_4(\text{CO})_{10}][(\text{GeCo}_2(\text{CO})_7)]$  (C).

(e) the first cluster with a trigonal bipyramidal core incorporating Ge,  $(\text{EtGe})_2\text{Fe}_3(\text{CO})_{19}$  (D)

The syntheses, characterisation, and structures of  $\text{A}_1, \text{A}_2, \text{A}_3, \text{A}_4, \text{B}_1, \text{C}$  and D will be presented.

(1) S.G. Anema, K.M. Mackay, L.C. McLeod, B.K. Nicholson & J.M. Whittaker, Angew. Chemie. Int. Ed. Eng., **25** (1986) 759 and refs therein.

(2) S.P. Foster, K.M. Mackay & B.K. Nicholson, Inorg. Chem., **24** (1985) 909

(3) P. Gusbeth and H. Vahrenkamp Chem. Ber. **118**, (1985) 1746



PHOTOCHEMISTRY OF METAL-METAL BONDED CARBONYLS WITH A LOWEST METAL TO LIGAND CHARGE-TRANSFER (MLCT) EXCITED STATE

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Although the photochemistry of unsubstituted metal-metal bonded carbonyls has been studied in detail,<sup>1</sup> much less attention has been paid to substituted binuclear carbonyls such as  $\text{XM}(\text{CO})_3(\alpha\text{-diimine})$  ( $\text{X}=\text{M}(\text{CO})_5$ ,  $\text{Co}(\text{CO})_4$ ,  $\text{CpFe}(\text{CO})_2$ ,  $\text{Ph}_3\text{Sn}$ ;  $\text{M}=\text{Mn}, \text{Re}$ ;  $\alpha\text{-diimine}=\text{bpy}$ , phen etc.), which possess an extra metal to  $\alpha\text{-diimine}$  charge-transfer (MLCT) band in the visible region. Contrary to most mononuclear complexes with a lowest MLCT state, these  $\text{XM}(\text{CO})_3(\alpha\text{-diimine})$  compounds are photoreactive showing both homolysis of the metal-metal bond and release of  $\text{CO}$ .<sup>2</sup> The radicals  $\text{M}(\text{CO})_3(\alpha\text{-diimine})$ , formed by the homolysis reaction, have been identified as stable 16e-radical complexes with ESR and IR for  $\text{M}=\text{Re}$ . The corresponding  $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})$  radicals can act as catalysts in electron transfer catalyzed reactions. Examples of such reactions will be given. The  $\alpha\text{-diimines}$   $\text{R-PyCa}$  (=pyridine-2-carbaldehyde imine) and  $\text{R-DAB}$  (=1,4-diaza-1,3-butadiene) afford novel complexes  $\text{Mn}(\text{CO})_4(\sigma, \sigma, \eta^2\text{-R-PyCa})\text{Mn}(\text{CO})_3$  and  $\text{Mn}(\text{CO})_3(\sigma, \sigma, \eta^4\text{-R-DAB})\text{Mn}(\text{CO})_3$ , respectively, by reaction of the  $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})$  and  $\text{Mn}(\text{CO})_5$  radicals. Exceptional reactions are also observed for the complexes  $(\text{CO})_4\text{CoRe}(\text{CO})_3(\alpha\text{-diimine})$  and  $\text{Ph}_3\text{SnMn}(\text{CO})_3(\alpha\text{-diimine})$ . The  $\text{Co-Re}$  complexes produce  $\text{Re}(\text{CO})_3(\alpha\text{-diimine})^+\text{Co}(\text{CO})_4^-$  and the  $\text{Sn-Mn}$  complexes lose  $\text{CO}$  with high quantum yield even upon irradiation with  $\lambda=600\text{nm}$ .

The mechanisms of these reactions will be discussed.

#### References

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- 2) D.J. Stufkens, 'Steric and Electronic Effects on the Photochemical Reactions of Metal-Metal bonded Carbonyls', in 'Stereochemistry of Organometallic and Inorganic Compounds', Vol.3, Ed. I. Bernal, Elsevier 1988.

# INFRARED FREQUENCIES AND INTENSITIES OF ALKYNES COORDINATED ON METAL CLUSTERS.

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Alkynes provide a great structural and chemical variety in the interactions with transition metals in complexes<sup>1</sup>. It is noteworthy their ability to bind simultaneously two, three or four metal atoms with largely different  $\sigma$ - $\pi$  interaction and significant rehybridization of the acetylenic carbon atom. Vibrational spectroscopic properties of the coordinated alkyne may be related to the nature of the metal-ligand bond; moreover, if the surface-coordination chemistry analogy is valid, the comparison with the spectral data of the alkyne adsorbed on a surface can offer useful insights about the structure of the chemisorbate.

Systems belonging to the series  $\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')$ ,  $\text{Os}_3(\text{CO})_{10}(\text{RC}_2\text{R}')$  and  $\text{Co}_4(\text{CO})_{10}(\text{RC}_2\text{R}')$  with  $\text{R}=\text{R}'=\text{H}, \text{CH}_3$  and  $\text{R}=\text{H}, \text{R}'=\text{CH}_3$ , with alkyne coordination of the type  $\mu\text{-}\eta^2, \mu_3\text{-}\eta^2, \mu_4\text{-}\eta^2$  and metal-alkyne bond formally  $\pi_2, \sigma_2\pi, \sigma_2\pi_2$ , were studied. The frequencies associated with the main vibrational modes of the alkynes (in particular,  $\text{C}\equiv\text{C}$  and  $\text{C-H}$  stretchings and  $\text{C-H}$  deformations) were evaluated with respect to those of the free alkyne and to the coordination type. At the same time, the contribution per the  $\text{C-H}$  bond to the total intensity in the  $\text{C-H}$  stretching and deformation region was measured: this is known to be easily related with the electrical properties of the  $\text{C-H}$  bonds in different surroundings<sup>2</sup>. Both the frequency and intensity data provide informations on the effect induced by the kind of coordination to the metal atoms (structure of the cluster, different  $\sigma$  and  $\pi$  contribution to the bond) on the geometry and on the charge distribution in the alkyne.

ACKNOWLEDGMENT P.L.S. thanks NATO for a grant.

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EFFECT OF STRUCTURE ON THE RELATIVE REACTIVITY OF STYRENES BY  
DIIDOBORANE-METHYL SULFIDE

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We have examined the properties and the reactivity of a new hydroborating agent,  $\text{HBI}_2 \cdot \text{SMe}_2$ , which is prepared by reacting  $\text{BI}_3$  and  $\text{BH}_3 \cdot \text{SMe}_2$  in the appropriate molar ratio. Diiodoborane is more sensitive than dibromoborane to moisture and this makes its preparation more difficult. It appears to be indefinitely stable at room temperature when stored under nitrogen. Ethereal solvents cannot be used for  $\text{HBI}_2 \cdot \text{SMe}_2$  since cleavage of the ether linkage occurs at a significant rate.

The reactivity of  $\text{HBI}_2$  is lower than that of  $\text{HBBr}_2$ . For example, 1-octene is hydroborated in  $\text{CH}_2\text{Cl}_2$  at  $25^\circ$  by  $\text{HBI}_2$  to the extent of 60% in 4 hrs, while hydroboration with  $\text{HBBr}_2$  in the same experimental conditions reaches 69% in 1 h. For *cis*-3-octene the results are as follows:  $\text{HBI}_2$ , 36% in 1 hr;  $\text{HBBr}_2$ , 87% in 1 hr.

In order to establish the role of electronic effects in influencing the directions of addition of the boron-hydrogen moiety to the carbon-carbon double bond, a number of para-substituted styrenes,  $\text{X}-\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$  ( $\text{X} = \text{H}$ ,  $\text{CH}_3\text{O}$ ,  $\text{CH}_3$ ,  $\text{Cl}$ ,  $\text{CF}_3$ ,  $\text{NO}_2$ ), were hydroborated with  $\text{HBI}_2 \cdot \text{SMe}_2$  under standard conditions ( $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ). The alcohols produced in the oxidation of the organoboranes were analyzed by gas-chromatography to establish the isomeric distribution. It is of interest that in the cases of 4-nitro- and 4-trifluoromethylstyrene major amounts of the corresponding ethylbenzenes were formed.

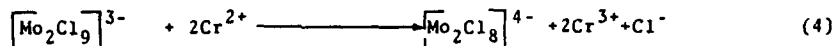
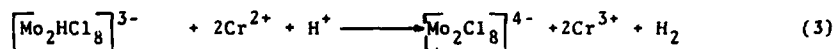
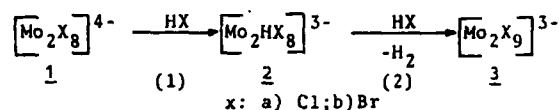
The results show that electron-withdrawing groups favour the addition of boron to the  $\alpha$ -position (for  $\text{X} = \text{Cl}$ ,  $\text{CF}_3$ ,  $\text{NO}_2$  the % of  $\alpha$ -ol is 39, 56, 67, respectively), while the electron-releasing groups favour the addition of boron to the  $\beta$ -position (for  $\text{X} = \text{CH}_3\text{O}$  only 2-(para-methoxyphenyl)ethanol is formed). This behaviour is in agreement with the four-centred transition state proposed by Brown. It is also of interest to point out that the effect of these substituents in influencing the direction of the hydroboration parallels qualitatively their  $\sigma^+$  values. Indeed, a plot of  $\log(k_\beta/k_\alpha)$  against  $\sigma^+$  reveals a reasonably good linear relationship and shows that  $\text{HBI}_2$  is extremely sensitive to electronic effects.

Finally, the unexpected large formation of substituted ethylbenzenes for 4-nitro- and 4-trifluoromethylstyrenes is probably due to a base-catalyzed deboronation which involves the formation of carbanionic intermediates, stabilized by the electron-withdrawing substituents.

A mechanistic study of HX (X=Cl,Br) addition to the  $[\text{Mo}_2\text{Br}_8]^{4-}$ ,  $[\text{Mo}_2(\mu\text{-H})(\mu\text{-X})_2\text{X}_6]^{3-}$ , X=Cl,Br ions and the homogeneous reduction of  $[\text{Mo}_2(\mu\text{-X})_3\text{X}_6]^{3-}$  X=Cl,Br by aqueous Cr(II).

Constantinos Mertis, Maria Chorianopoulou, Spyros Koinis, Myrsini Cravaritou and Nikos Psaroudakis.

Low-valent metal ions like  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$  and  $\text{Eu}^{2+}$  give dihydrogen at relatively slow rates even at HCl concentrations as high as 12M. However, the reaction is considerably accelerated in the presence of multiply bonded dimolybdenum complexes forming hydrides (eq.(1) and (2))<sup>1</sup> which then react with the reducing metal ion eq.(3) and (4)<sup>2</sup>:



We now report an extension of these studies including also the analogous bromo-derivatives which are extremely more reactive than their chloro counterparts. The rates of the reactions (1) and (2) are first order in  $\text{H}^+$  and the  $\text{Mo}_2^{4+}$  reactants.

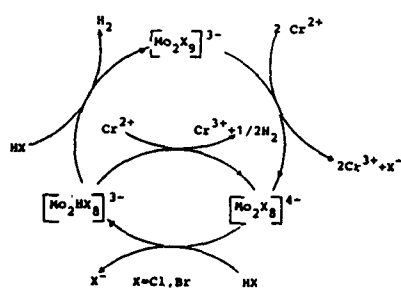


Figure 1

Table I

Reaction	$E_a$ (KJ mol <sup>-1</sup> )
(1)	80.5 (X=Cl), 33.0 (X=Br) (no compound)
(2)	71.9 "

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ELIMINATION OF ACID HALIDES FROM ACETYL, PHENYLACETYL,  
AND BENZOYL CHLOROBIS(TRIPHENYLPHOSPHINE) PLATINUM(II)  
AND PALLADIUM(II) COMPLEXES.

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Oxidative addition and migratory insertion reactions which are important basic steps in homogeneously catalyzed reactions of carbon monoxide such as in the Monsanto acetic acid and Eastman acetic anhydride synthesis have been extensively studied, but reductive elimination of acid halides has not been investigated in depth. Attempts to reductively eliminate acid halides usually lead to decarbonylation and elimination of the alkyl halide. The reactions of the acyl metal complexes  $[M(PPh_3)_3Cl(RCO)]$ , 1, where M is Pt or Pd and R is  $CH_3$ ,  $PhCH_2$ , or Ph with the halogens ( $X_2$ ) chlorine, bromine, or iodine yield the acid halides  $RCOX$ . Reactions of the acyl complexes, 1, with  $ICl$  give the acid chlorides  $RCOCl$ . The rates of the reactions are too rapid to be measured by standard techniques, and no intermediates were detected at temperatures above 168 K. Mechanisms for the elimination reactions will be discussed.

FLASH PHOTOLYSIS INVESTIGATIONS OF RHODIUM AND IRIDIUM  
PHOSPHINE COMPLEXES

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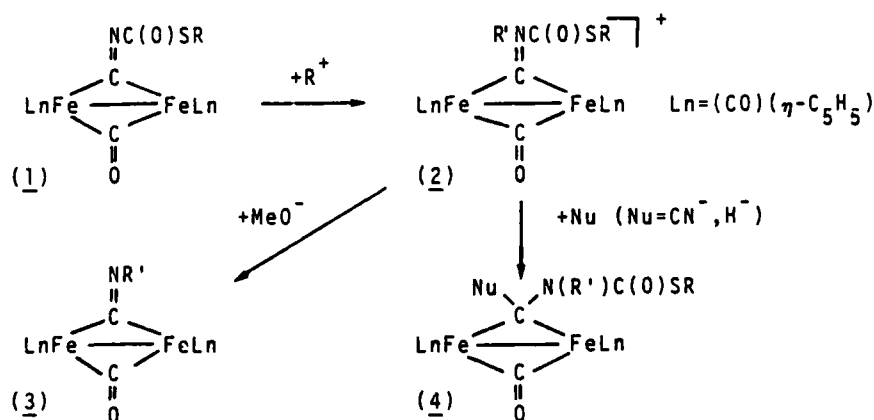
Flash photolysis techniques have been used to investigate photodissociation pathways and reactions of transient intermediates. The kinetics displayed by such transients formed from tetracoordinate complexes such as  $\text{RhCl}(\text{CO})\text{dppe}$  ( $\text{dppe}$ =1,2-bis(diphenylphosphino)ethane)  $\text{IrCl}(\text{CO})\text{dppe}$ ,  $\text{trans-RhCl}(\text{CO})(\text{tri-p-tolylphosphine})_2$ , and other such analogs offer information regarding the nature of these intermediates. The kinetics observed with flash photolysis techniques of these and other  $\text{Ir}(\text{I})$  and  $\text{Rh}(\text{I})$  phosphine complexes will be discussed and related to possible mechanisms of reaction for the transient intermediates formed.

## CHEMISTRY OF BRIDGING ACYL ISOCYANIDE COMPLEXES

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The novel bridging acyl isocyanide complexes (1), recently synthesized by  $\text{NCO}^-$  insertion into the C-S bond of  $[(\text{Cp})_2(\text{CO})_3\text{Fe}_2(\mu\text{-CSR})]^+$  ( $\text{R} = \text{Me}, \text{Et}$ ;  $\text{Cp} = \eta\text{-C}_5\text{H}_5$ ), readily undergo N-alkylation or N-protonation to form stable cationic imminium-bridged derivatives (2:  $\text{R}=\text{R}'=\text{Me}, \text{Et}$ ;  $\text{R}=\text{Et}, \text{R}'=\text{Me}$ ).

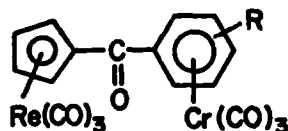
$\text{NaOMe}$  in methanol converts (2) into the known bridging isocyanide derivatives (3:  $\text{R}'=\text{Me}, \text{Et}$ ) via N-C(O)SR bond cleavage. The electrophilic nature of the bridging carbyne-like carbon atom in (2) is demonstrated from the reactions with nucleophiles ( $\text{CN}^-$ ,  $\text{H}^-$ ) which afford bridging carbene derivatives (4). The results of studies concerned with the stereochemistry of the above reactions together with other aspects of the reactivity of type (1) complexes, will be reported.



## SYNTHESIS AND SPECTROSCOPIC STUDIES OF MIXED Re AND Cr CARBONYL COMPLEXES

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A series of benzoylcyclopentadienyl complexes have been prepared in which the cyclopentadienyl ring is complexed by a  $\text{Re}(\text{CO})_3$  group and the benzene ring by a  $\text{Cr}(\text{CO})_3$  group.



$\text{R} = \text{H}, \text{o-CH}_3, \text{p-CH}_3, \text{p-OCH}_3, \text{o-F}, \text{p-Cl}$

The complexes have been studied by IR,  $^1\text{H}$  NMR and mass spectrometry. Similar studies on the parent  $\text{Re}(\text{CO})_3$  complexes have been carried out for comparison. Substituents on the benzene ring affect the ketonic  $\nu_{\text{CO}}$  and  $\nu_{\text{CO}} [\text{Cr}(\text{CO})_3]$  but not  $\nu_{\text{CO}} [\text{Re}(\text{CO})_3]$ .

Comparison with results for similar Mn complexes<sup>1</sup> reveals significant differences between the two series. The  $\nu_{\text{COs}}$  of  $\text{Re}(\text{CO})_3$  are lower by 5-12  $\text{cm}^{-1}$  than the  $\nu_{\text{COs}}$  of  $\text{Mn}(\text{CO})_3$ . On average the  $\nu_{\text{COs}}$  of  $\text{Cr}(\text{CO})_3$  are higher for the Re complexes than for the Mn complexes. The reasons for the observations and for observed changes in  $^1\text{H}$  NMR shifts are explained by differences in the electron-withdrawing ability of the  $\text{M}(\text{CO})_3$  groups.

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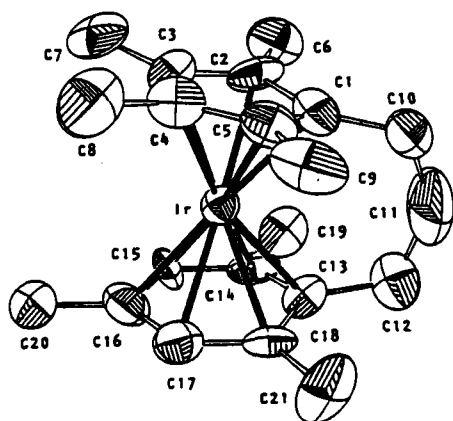
CRYSTAL AND MOLECULAR STRUCTURE OF TWO Iridium(II) CYCLOPHANES:  
 $[\text{Ir}(\eta^{11}\text{-C}_5\text{Me}_4\text{C}_3\text{H}_6\text{C}_6\text{H}_2\text{Me}_3)](\text{BF}_4)_2(\text{MeNO}_2)$  AND  $[\text{Ir}(\eta^{11}\text{-C}_5\text{Me}_4\text{C}_3\text{H}_6\text{C}_6\text{H}_2\text{Me}_3)](\text{BF}_4)_2(\text{MeOH})$

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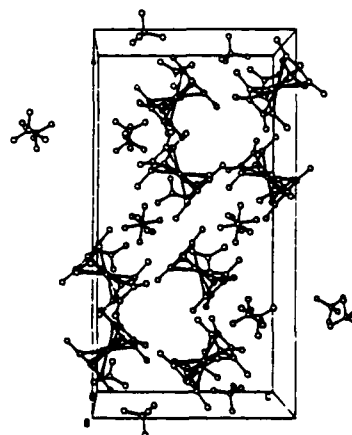
V.S. Kaganovich, R.R. Kudinov and M.I. Rybinskaya, A.N. Nesmeyanov Institute of Organo-Element Compounds of the Academy of Sciences of the USSR, Vavilov St. 28, Moscow 117334, U.S.S.R.

The structures of the compounds  $[\text{Ir}(\eta^{11}\text{-C}_5\text{Me}_4\text{C}_3\text{H}_6\text{C}_6\text{H}_2\text{Me}_3)](\text{BF}_4)_2(\text{MeNO}_2)$  (1) and  $[\text{Ir}(\eta^{11}\text{-C}_5\text{Me}_4\text{C}_3\text{H}_6\text{C}_6\text{H}_2\text{Me}_3)](\text{BF}_4)_2(\text{MeOH})$  (2) have been determined by X-ray diffraction. The compound 1 crystallizes in space group  $Pb\bar{c}n$  ( $Z = 8$ ) with  $a$  26.812(18),  $b$  14.275(11),  $c$  13.942(5) Å, and the compound 2 in the space group  $Pnma$  ( $Z = 4$ ) with  $a$  28.313(6),  $b$  9.137(3),  $c$  9.789(4) Å. The two structures are similar, bridged sandwich complexes, with an Ir atom bonded to the cyclopentadienyl and benzene rings of the organic ligand. The solvent molecules  $\text{MeNO}_2$  and  $\text{MeOH}$  and the  $\text{BF}_4^-$  anions are more or less disordered in the structures, but they could be located from the difference Fourier maps. The Ir complex cations form discrete units in both structures. The crystal structures are thermally rather labile and are held together mainly through van der Waals forces.

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An ORTEP drawing of the  $[\text{Ir}(\eta^{11}\text{-C}_5\text{Me}_4\text{C}_3\text{H}_6\text{C}_6\text{H}_2\text{Me}_3)]^{2+}$  cation (with 295 K parameters) of 1 showing the ion geometry and the atom numbering scheme. Thermal ellipsoids are drawn at 50% probability level for the non-H atoms.



Molecular packing in the unit cell of  $[\text{Ir}(\eta^{11}\text{-C}_5\text{Me}_4\text{C}_3\text{H}_6\text{C}_6\text{H}_2\text{Me}_3)](\text{BF}_4)_2(\text{MeNO}_2)$  viewed down  $b$ .

THE TRANSIENT RADICAL ANIONS  $\text{Fe}(\text{CO})_4^-$  AND  $\text{M}(\text{CO})_5^-$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ): ELECTRON SPIN RESONANCE, ELECTROCHEMISTRY AND MO CALCULATIONS

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The solution ESR spectra of the transient radical anions  $\text{Fe}(\text{CO})_4^-$  (1) and  $\text{Cr}(\text{CO})_5^-$  (2),  $\text{Mo}(\text{CO})_5^-$ , and  $\text{W}(\text{CO})_5^-$  are reported and discussed together with their anisotropic spectra in frozen 2MeTHF glasses. The radicals are produced by photochemical cleavage of the metal-metal bond in  $\text{Na}_2\text{Fe}_2(\text{CO})_8$  and  $\text{K}_2\text{M}_2(\text{CO})_{10}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) in THF. The ESR parameters are consistent with  $\text{C}_{3v}$  and  $\text{C}_{4v}$  geometries for  $\text{Fe}(\text{CO})_4^-$  and the  $\text{M}(\text{CO})_5^-$  radicals, respectively, which are also the geometries of the prototypical radicals  $\text{Co}(\text{CO})_4$  and  $\text{Mn}(\text{CO})_5$ , isoelectronic with 1 and 2. The remarkable similarity of the electronic and geometric structures of these radicals is also brought out by Extended Hückel MO calculations which reveal substantial delocalization of the unpaired electron onto the basal CO ligands (ca. 50%). The  $\text{Cr}(\text{CO})_5^-$  radical exchanges very rapidly its CO ligands with  $^{13}\text{CO}$ , and the ESR spectra of the  $^{13}\text{C}$  isotopomers indicate that the five CO ligands are rendered equivalent in solution on the ESR time scale by a fast intramolecular exchange process. Cyclic voltammetry with microelectrodes in the absence of supporting electrolyte shows that at sufficiently rapid potential scans 1 can be generated reversibly by oxidation of  $\text{Fe}(\text{CO})_4^{2-}$ . 1 is not an important intermediate in the electrochemical reduction of  $\text{Fe}(\text{CO})_5$  as currently believed. The reduction of the latter is a two-electron process leading directly to  $\text{Fe}(\text{CO})_4^{2-}$  which reacts rapidly with  $\text{Fe}(\text{CO})_5$  to yield  $\text{Fe}_2(\text{CO})_8^{2-}$ , the major product of electrolysis. An analysis of the cyclic voltammograms yields the rate of this reaction ( $6 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ). In the anodic potential scan,  $\text{Fe}_2(\text{CO})_8^{2-}$  is reversibly oxidized to the radical anion  $\text{Fe}_2(\text{CO})_8^-$  whose ESR behavior will also be briefly discussed.

# CHEMISTRY AND STRUCTURE OF ARYLDIFLUOROPHOSPHINE PLATINUM(II)-COMPLEXES CONTAINING Pt-C BONDS

Lutz Heuer, Ludger Ernst, Reinhard Schmutzler

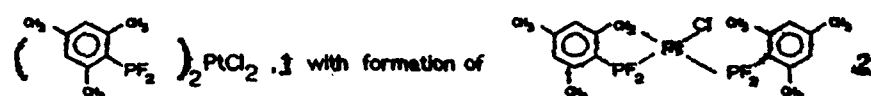
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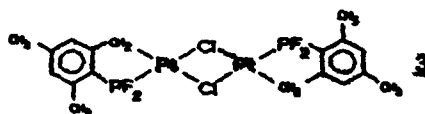
During our investigations on platinum(II) complexes of type *cis*-dichloro-bis(aryldifluorophosphine)platinum(II)<sup>1,2</sup> we have observed the elimination reaction of HCl in the compound



The identity of **2** was established by <sup>1</sup>H-, <sup>13</sup>C-, <sup>19</sup>F-, <sup>31</sup>P- and <sup>195</sup>Pt-n.m.r. spectroscopy. In contrast to the n.m.r. spectra for all the other nuclei and even without proton decoupling the <sup>195</sup>Pt-n.m.r. spectrum could be interpreted on a first order basis. The structure of **2** has also been established by a single crystal X-ray diffraction study.

As a byproduct in the preparation of

**2** compound **3** was observed.



The unusually short Pt-P bond (212 pm), found in the single crystal X-ray diffraction study of **3** is reflected in the very large <sup>1</sup>J(PtP) coupling constant (7646 Hz).

The reaction of **2** with SeMe<sub>4</sub> and HgPt<sub>2</sub> lead to the formation of **4** and **5**, respectively.



These complexes are the first involving *trans* PF<sub>2</sub> groups. Therefore, in the <sup>31</sup>P-n.m.r. spectra small <sup>1</sup>J(PtP) coupling constants were detected. A correlation between the Pt-P bond length and <sup>1</sup>J(PtP) has been found to be obeyed by **2** and **3**.

<sup>1</sup> L.Heuer, M.Seil, R.Schmutzler, and D.Schomburg, *Polyhedron*, **1987**, *6*, 1295.

<sup>2</sup> L.Heuer and R.Schmutzler, *J.Fluorine Chem.*, **1988**, *39*, 197.

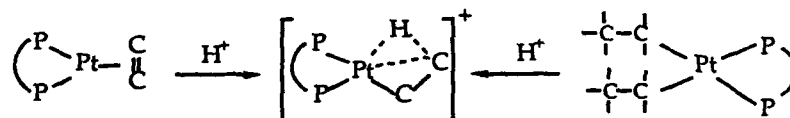
# β-AGOSTIC COMPOUNDS OF PLATINUM AND PALLADIUM

Nicholas Carr,<sup>a,b</sup> Barry J Dunne,<sup>b</sup> Laura Mole,<sup>a</sup> A Guy Orpen<sup>b</sup> and John L Spencer<sup>a</sup>

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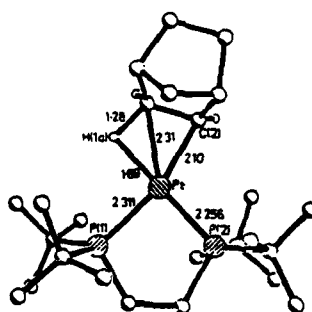
<sup>b</sup> Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, UK

The protonation of 16-electron platinum and palladium alkene complexes [ML<sub>2</sub>(alkene)] (M = Pt, Pd; L<sub>2</sub> = chelating diphosphine; alkene = C<sub>2</sub>H<sub>4</sub>, norbornene etc) affords a series of cationic alkyl complexes in which the electronic requirements of the nominally 14-electron metal centre are satisfied by interaction with a β-C-H bond of the alkyl group (an *agostic* interaction). The same compounds may be made by the protonation of platinum dialkyls through the elimination of alkane.



This system has proved to be particularly suitable for study by multinuclear nmr methods, and the spectroscopic results correlate well with the results of single crystal X-ray diffraction studies. The norbornyl complex [PtC<sub>7</sub>H<sub>11</sub>(Bu<sup>t</sup><sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PBu<sup>t</sup><sub>2</sub>)]BPh<sub>4</sub> (Figure) is typical of several which have been characterised. Interestingly the extent of the 3-centre, 2-electron agostic interaction is controlled by the bite angle of the phosphine.

Platinum complexes with agostic alkyl groups undergo extremely facile intramolecular rearrangements and are also reactive in an intermolecular sense.

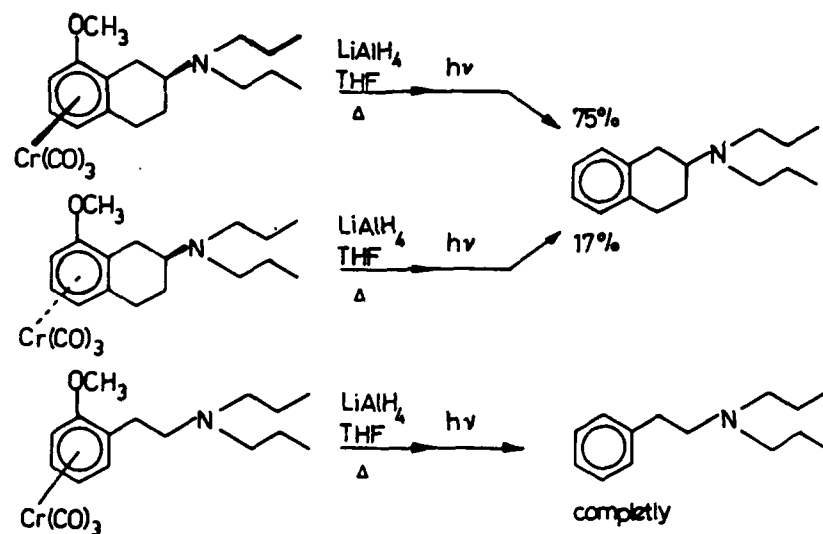


$\eta^6$  - CROMIUMTRICARBONYL COMPLEX INTERMEDIATES IN SYNTHESIS  
OF TETRAHYDRONAPHTHALENE DERIVATIVES

Marie Persson and Uli Hacksell, Department of Organic  
Pharmaceutical Chemistry, University of Uppsala, S-751 23  
Uppsala, Sweden

Ingeborg Csöreg, Department of Structural Chemistry,  
Arrhenius lab., University of Stockholm, S-106 91 Stockholm,  
Sweden

We have observed that hydride can act as a nucleophile, dis-  
placing aromatic methoxy groups on some  $\text{Cr}(\text{CO})_3$ -complexed  
amino-substituted tetralins and related compounds.



Mechanism, scope and limitations of the reaction will be  
discussed.

**New Studies of C-H Bond Activation Reactions Using Complexes of Rhodium.**

William D. Jones, Valerie L. Chandler, and Lingzhen Dong, Department of Chemistry, University of Rochester, Rochester, New York, 14627, USA.

A variety of complexes of the general formula  $(C_5Me_5)Rh(PR_3)(Ar)H$  have been prepared by C-H bond activation of the appropriate arene. For complexes with  $R = Me$ , aromatic species including substituted benzenes, naphthalenes, furans, and pyroles have been examined. Several unusual rearrangements have been observed in the course of this chemistry, indicating a new type of C-H bond activation that does not involve the 16-electron  $[(C_5Me_5)Rh(PMe_3)]$  intermediate.

The complexes with  $PR_3 = PMe_2Ph, PMePh_2, PPh_3, P(t-Bu)_3, PCy_3, P(n-Bu)_3, PMe_2(n-Pr), PCH_2Ph$ , and  $PMe_2Bu$  have been prepared and reactions with  $H_2$  studied. The stability of the phenyl hydride complexes were found to vary with both steric and electronic differences in the phosphine ligand. Evidence for the intermediacy of  $Rh(V)$  intermediates in the hydrogenolysis was also found. Intramolecular reactions of the phosphine ligand were also observed and the stability of these species will be compared with the intermolecular activation adducts.

Reactions of the complex  $(C_5Me_5)Rh(PMe_3)(Ph)H$  with a variety of electrophiles ( $CS_2, PhNCS, MeOCC\equiv CCOOMe$ ) have also been examined. In all cases insertion into the metal-hydrogen bond is observed. With the sulfur containing substrates, a series of complex thioacetal reactions are seen in the organic ligands while bound to the metal.

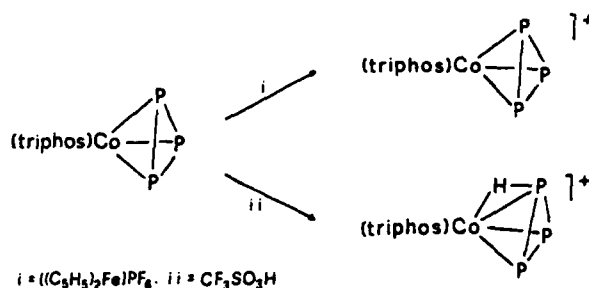
# REACTIVITY OF "MIXED" METAL-NAKED PHOSPHORUS CLUSTER COMPOUNDS

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Università di Firenze, Via Maragliano, 77, I-50144 Firenze, Italy  
Stefano Midollini, Maurizio Peruzzini, Istituto I.S.S.E.C.C., CNR,  
Via J. Nardi, 39, I-50132 Firenze, Italy

Piero Zanello, Dipartimento di Chimica, Università di Siena,  
Pian de' Mantellini, 44, I-53100 Siena, Italy

The cluster compounds  $[M^*P_3]$  [ $M^* = C_5Me_5Mo(CO)_2$ ,  $(CO)_3Co$  and  $(triphos)M$ ; triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane;  $M = Co, Rh, Ir$ ] and  $[M^*P_2X]BF_4$  [ $M^* = (triphos)Co$ ;  $X = S, Se$ ], which contain unsubstituted main group atoms and metal fragments in a pseudotetrahedral geometry, present non-bonding electrons available for redox processes and for interactions with electrophilic reagents or transition-metal ligand units. While the reactivity of such species toward metal fragments has been considered,<sup>1</sup> scarce attention has been addressed to their chemistry with oxidizing or electrophilic reagents.

The compound  $[(triphos)CoP_3]$  reacts with  $[(C_5H_5)_2Fe]PF_6$  yielding the paramagnetic monocation  $[(triphos)CoP_3]PF_6$  ( $\mu_{eff} = 2.11$  BM).



Trifluoromethansulphonic acid reacts with the cobalt derivative affording a compound of formula  $[(triphos)CoP_3H](H_2O)(CF_3SO_3)_2 \cdot H_2O$ . The deformations undergone by the  $CoP_3$  core in the  $[(triphos)CoP_3H]^+$  cation, as shown by an X-ray analysis, suggest that the hydrogen atom bridges the cobalt and one phosphorus atom.  $^1H$  and  $^{31}P$  n.m.r. data obtained at different temperatures point to rapid exchange of the hydrogen with the solvent.

Work supported by Ministero Pubblica Istruzione (MPI, Roma).

1 M. Di Vaira, M. Peruzzini, and P. Stoppioni, Polyhedron, 6, 351, 1987.

REVERSAL OF SELECTIVITY IN SE<sub>2</sub> CLEAVAGE OF MIXED ORGANOTIN  
COMPOUNDS BY HALOGENS

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Libération, 33405 - Talence Cedex (France)

Numerous data on electrophilic cleavage of metal-carbon bonds is now available. These studies have been developed primarily because the very high selectivity of electrophilic demetallation allows usefull synthetic applications. The ease of cleavage by halogens of mixed organotin derivatives follows the sequence : benzyl > aryl  $\approx$  vinyl > methyl > higher alkyl. For mixed tetraalkyltin compounds, a cyclic or an open S<sub>E</sub>2 transition state, or a charge-transfer mechanism has been proposed to account for selectivity, solvent effects and configurationnal changes at the cleaved organic group, whereas an open S<sub>E</sub>2 transition state with assistance of the solvent or another molecule of electrophile is generally accepted for aryl or vinyltin derivatives.

We present the first exemples of halogenodemetallation<sup>1</sup> where the usual sequence of reactivity is reversed, i.e. where alkyl groups are cleaved preferentially to aryl, vinyl or benzyl groups in mixed tetraorganotin derivatives and propose an interpretation of these very unexpected results.

1-B.Jousseume,P.Villeneuve,J.Chem.Soc.Chem.Commun.1987,517.



## TIN-CARBON BONDED CARBOHYDRATE DERIVATIVES

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University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE

Carbohydrate derivatives containing tin-carbon bonds have been synthesized by standard routes, including reactions of  $R_3SnLi$  with carbohydrates having tosylate, carbonyl or epoxy groups.

Transmetallation reactions of the tin derivatives have been attempted with chloro-platinum and -palladium complexes as well as with organolithium reagents. Reactions with electrophilic reagents (e.g. halogens and proton acids) have also been studied.

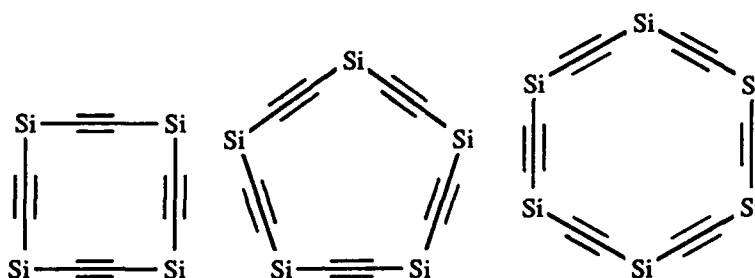
The metallated carbohydrates have some potential in carbohydrate synthesis.

**Pericyclynosilanes : Synthesis of a New Class of Cyclic Organosilicon Compounds.**

**Roberto Bortolin, Bhukan Parbhoo and Scott S.D. Brown**

*Dow Corning Research Group, School of Molecular Sciences, The University of Sussex, Brighton BN1 9Qj, UK*

Pericyclynosilanes are cyclic compounds composed of alternating  $R_2Si$  and  $C\equiv C$  units.



They can be prepared in high yields by reaction of  $R_2Si(C\equiv CH)_2$ , BuLi and  $R_2SiCl_2$  according to the following scheme:



The combination of substituents R on the silicon of the reagents allows the synthesis of a large number of pericyclynosilanes, each one in different ring sizes. The compounds  $(Me_2SiC\equiv C)_6$  and  $(Ph_2SiC\equiv C)_6$  have been isolated and structurally characterized by X-ray crystallography.

The synthesis of pericyclynosilanes allows the demonstration of a novel rearrangement mechanism occurring on the silicon. The species responsible for such rearrangements were identified. Pericyclynosilanes can be coordinated to metal centers such as copper.

**WEAK INTERACTIONS IN ORGANOMETALLIC COMPOUNDS:  
STRUCTURAL CRITERIA**

Gerhard Müller, Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstr. 4, D-8046 Garching, FRG.

Extensive structural, spectroscopic, and theoretical studies make hydrogen bonds probably the best understood weak intra- and intermolecular interactions, both in solution and in the solid state. From structural studies in particular, detailed geometrical criteria can be given for hydrogen bonds. Other weak interactions are less amenable to such a systematic treatment. Ion-induced dipole interactions, closed-shell ( $d^{10}$ - $d^{10}$ ) attractive interatomic interactions, and particularly London dispersion (van der Waals) forces are typical examples for this situation.

On the basis of a large number of crystal structures on various classes of organometallic compounds evidence for common features of weak interactions has been established. In particular, weak electrostatic interactions are shown to have a decisive influence on the structures of organolithium compounds, while closed-shell interactions between  $Au(d^{10})$  centers may be substantiated by a comparison of the ground state conformations of their P ylide complexes and those of the respective free ligands. Ample structural evidence for van der Waals forces and weak ion-induced dipole attraction is found in the complexes of  $Ga(I)$ ,  $In(I)$ , and  $Tl(I)$ , as well as  $AsX_3$ ,  $SbX_3$ , and  $BiX_3$  ( $X$  = halogen), with uncharged arenes, most notably with substituted benzenes.

STRUCTURE AND DYNAMIC BEHAVIOR OF SOLVATED  
ORGANOLITHIUM COMPOUNDS

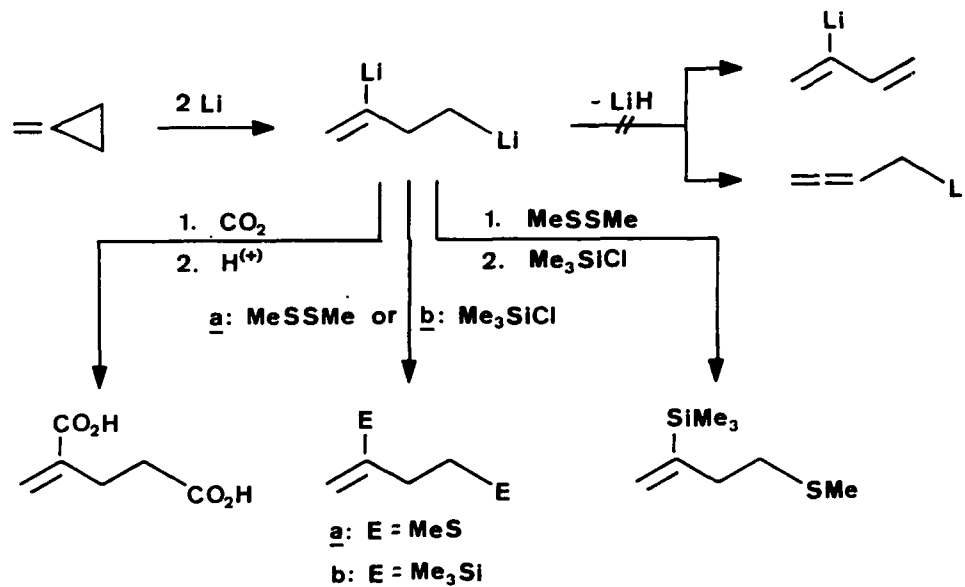
Gideon Fraenkel, Department of Chemistry, Ohio State University,  
120 W. 18th Avenue, Columbus, Ohio 43210, USA.

If there is observable spin coupling between  $^{13}\text{C}$  and directly bonded  $^6\text{Li}$  in organolithium compounds one can infer information about aggregate structure from the multiplicity of the  $\alpha$ -carbon resonance while from its averaging kinetic investigations can be made of interaggregate carbon lithium bond exchange. In this general way we have found out that  $(\text{RLi})_n$  species solvated by ethers or  $t$ -amines exist as equilibrium mixtures of bridged dimers, cubic tetramers and less frequently, monomers, the coordination number of lithium being four in all these species. In general, cooling these equilibrium mixtures favors the smaller aggregates because lithium therein is coordinated to more ligand molecules. Data for typical solvated organolithium compounds will be discussed. In particular we have investigated lithium  $t$ -butyl acetylide, a stable model system, in the presence of a wide variety of potential ligands. Simple ethers and monoamines give rise of tetramers whereas vicinal diamines favor dimers due to bidentate solvation of lithiums. The averaging of the  $^{13}\text{C}$ ,  $^6\text{Li}$  coupling, due to interaggregate carbon lithium bond exchange has been analyzed using our methods of NMR line-shape analysis which incorporate the mechanism of exchange into the density matrix equations which are solved to obtain the NMR absorption. Using these procedures we find the mechanism of exchange is the fast reversible dissociation of tetramer to dimers.

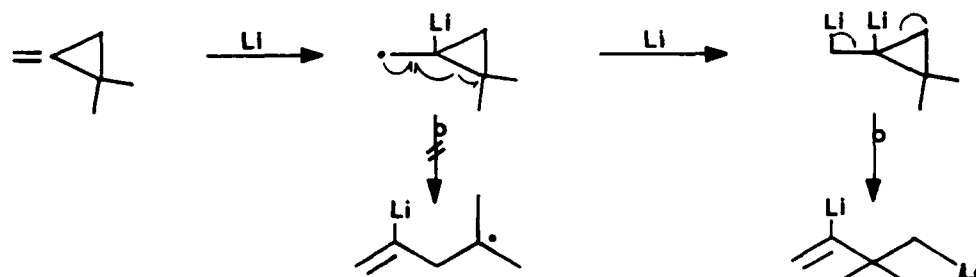
STABLE RING-OPENED 1,3-DILITHIUM ORGANIC COMPOUNDS UPON THE REACTION  
OF METHYLENECYCLOPROPANES WITH LITHIUM METAL: 2,4-DILITHIO-1-BUTENES

A. Maercker and K.-D. Klein, Department of Organic Chemistry,  
University of Siegen, D-5900 Siegen (FRG)

Methylenecyclopropane readily reacts with lithium powder in diethyl ether at room temperature or without solvent at its boiling point ( $10^{\circ}\text{C}$ ) to yield the stable 2,4-dilithio-1-butene which - in contrast to 1,3-dilithiopropene - does not split off lithium hydride. The two lithium atoms can be replaced stepwise by different electrophiles, the allylcarbinyl center being more reactive than the vinyl center:



Mechanism :



## CHIRAL TIN(II) ORGANOMETALLIC SYSTEMS AS ENANTIODIFFERENTIATING REAGENTS

Massimo Falorni, Luciano Lardicci

Dipartimento di Chimica e Chimica Industriale della Facolta' di Scienze dell'Universita', via Risorgimento 35, I-56100 Pisa, Italy.

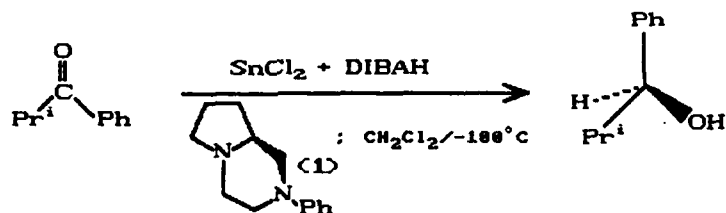
Giampaolo Giacomelli

Dipartimento di Chimica della Facolta' di Scienze dell'Universita', via Vienna 2, I-07100 Sassari, Italy.

Mauro Marchetti, Annamaria Piroddi

Istituto del CNR per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, via Vienna 2, I-07100 Sassari, Italy.

During our studies, we have reported that chiral reducing reagents can be obtained from optically active diamines and  $\text{LiAlH}_4$ .<sup>1</sup> In our present investigations on the asymmetric reductions of a wide variety of prochiral carbonyl substrates,<sup>2</sup> we discovered that a chiral organometallic system, generated from tin(II) chloride and diisobutyl aluminium hydride,<sup>3</sup> in the presence of a chiral diamine such as compound 1, reacts smoothly with prochiral ketones to yield the optically active secondary carbinol in good enantioselectivity.



In these reactions, the coordination of the bidentate chiral diamine to the bivalent tin atom plays an important role as shown from the use of  $\text{AlEt}_3$  instead of DIBAH. In this case, the reaction of the chiral tin system with benzaldehyde occurs to yield the alkylated carbinol in poor yield (<5%) in a very high enantiodifferentiating manner (e.e. >95%).

## References

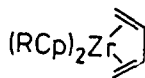
- 1) M. Falorni, L. Lardicci, G. Giacomelli, *Gazz. Chim. Ital.*, **1986**, *116*, 73.
- 2) M. Falorni, L. Lardicci, G. Giacomelli, *J. Org. Chem.*, **1986**, *51*, 2030.
- 3) T. Mukaiyama, K. Tomimori, T. Oriyama, *Chem. Lett.*, **1985**, 813.

Some Novel Structural and Chemical Aspects of Cp-substituted Bent  
Metallocene Complexes.

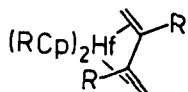
Gerhard Erker

Institut für Organische Chemie der Universität Würzburg  
Am Hubland, 8700 Würzburg (BRD)

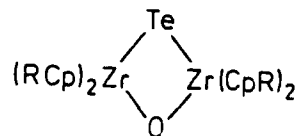
Preparations and properties of various examples of Cp-substituted group 4 bent metallocene complexes of general types  $(RCp)_2ML_n$  and  $(RCp)CpML_n$  are described. In the presence of sufficiently bulky Cp-substituents, chiral conformations of the bent metallocene unit are preferred in the solid state. In solution, often hindered RCp-M rotation is observed (typical examples are 1, 2, or 3).



1



2



3

The potential of the Cp-substituted group 4 metallocene complexes to serve as components in catalytically active systems is discussed.

REACTIVITY OF PARAMAGNETIC MONO- AND DICYCLOPENTADIENYL  
NIOBIUM DERIVATIVES

Abdenasser Zaki, Liliane G. Hubert-Pfalzgraf and Olivio Pagliarini,  
Laboratoire de Chimie Moléculaire, Associé au CNRS, Université  
de Nice, Parc Valrose, 06034 Nice, France

The molecular chemistry of low-valent niobium and tantalum derivatives remains limited, especially in oxidation state II.

Photochemical or chemical reduction of  $(\eta^5\text{-Cp})_2\text{NbMe}_2$  and  $(\eta^5\text{-Cp})_2\text{NbCl}_2$ , respectively, in the presence of trimethylphosphane, has been considered. The unusual lability of the niobium cyclopentadienyl linkage in some experimental conditions offers a route to  $(\eta^5\text{-Cp})\text{NbCl}_2(\text{PMe}_3)_2$ , **1**, a highly reactive paramagnetic species.

Its reactivity has been widely investigated (alkyl reagents, carbon monoxide, isocyanides, heterocumulenes, alkynes, diazabutadienes,...). **1** acts as a precursor for mono- as well as non-cyclopentadienyl niobium derivatives of various oxidation states, including oxidation state II. The synthesis and characterization of representative examples will be discussed.



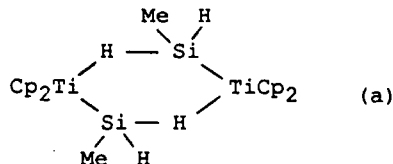
REACTIONS OF DIMETHYLTITANOCENE WITH  
ALKYL- AND ALKOXYSILANES.

E. Samuel, Ecole Nationale Supérieure de Chimie de Paris (UA 403 CNRS), 11 rue P. et M. Curie, 75005 Paris, France.

J. Harrod, Department of Chemistry, McGill University, Montreal, Canada.

Y. Drumzee, F. Robert and Y. Jeannin, Laboratoire de chimie des métaux de transition (ERA 608 CNRS), Université P. et M. Curie, 75005 Paris, France.

Dimethyltitanocene (I) reacts with  $\text{Me}(\text{OEt})_2\text{SiH}$  in toluene or hexane to yield the dimeric compound (a) containing Si-H bridges. The structure has been determined from H NMR by comparison with the previously reported compound<sup>1</sup>  $[\text{Cp}_2\text{TiSiH}_2\text{Ph}]_2$ .



In the presence of  $\text{PR}_3$  ( $\text{R}=\text{CH}_3, \text{C}_2\text{H}_5$ ), I gives with  $\text{PhSiH}_3$  the paramagnetic compound  $\text{Cp}_2\text{Ti}(\text{SiH}_2\text{Ph})\text{PR}_3$  (EPR:  $g=1.9944$ ;  $A(\text{P})=29.3\text{G}$ ;  $A(\text{H})=3.2\text{G}$ ). Preliminary crystal structure studies will be reported.

I also gives with  $(\text{OMe})_3\text{SiH}$  the dimeric paramagnetic compound  $[\text{Cp}_2\text{Ti}\mu-(\text{OMe})]_2$ . The EPR spectrum is characteristic of an excited triplet state. Crystal structure data will be reported.

1. C. Aitken, J. F. Harrod, E. Samuel, J. Amer. Chem. Soc., 1986, 108, 4059.

BI- AND TRI-NUCLEAR  $\eta^2$ -HYDRAZONATO  $\mu$ -OXO COMPLEXES OF TITANIUM

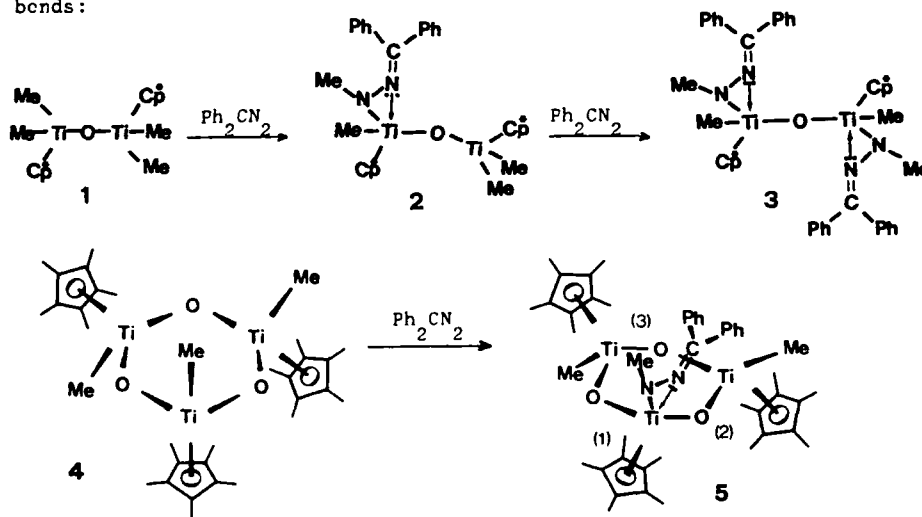
Juan Carlos Flores, Pascual Ryc, Ricardo Serrano, Miguel Mena

Departamento de Química Inorgánica, Universidad de Alcalá; Campus Universitario, 28871 Alcalá de Henares Madrid, Spain)

M.A. Fellinghelli, Antonio Tiripicchio

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Via M'Azeglio 85, I-43100 Parma, Italy.

We have recently described several di- and tri-nuclear  $\mu$ -oxo pentamethylcyclopentadienyl titanium dimers and trimers<sup>1</sup>; their reaction with diphenyldiazomethane has been investigated and lead to the formation of  $\eta^2$ -hydrazone complexes by insertion into the titanium-methyl bonds:



IR, NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) data as well as the X-ray structure of (2) are presented.

<sup>1</sup>S. García Blanco, M.P. Gómez Sal, S. Martínez Carreras, M. Mena, F. Ryc and R. Serrano, J. Chem. Soc. Chem. Commun. 1986; 1572

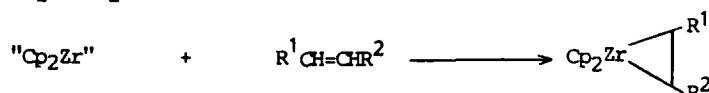
## PREPARATION AND REACTIONS OF ZIRCONACYCLOPROPANE COMPLEXES

Tamotsu Takahashi and Yasuzo Uchida, Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, JAPAN

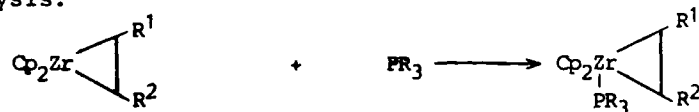
Tokiko Uchida, Department of Industrial Chemistry, Faculty of Science and Technology, The Science University of Tokyo, Noda, Chiba 278, JAPAN

Ei-ichi Negishi, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.

Zirconacyclopropane complexes were prepared by the reactions of olefins with zirconocene which was produced in situ from  $\text{Cp}_2\text{ZrCl}_2$  and 2 equiv of  $n\text{-BuLi}$ .



Addition of one equiv of  $\text{PR}_3$  to the complex ( $\text{R}^1 = \text{R}^2 = \text{Ph}$ ) gave yellow crystals. Its structure was determined by the X-ray analysis.



These zirconacyclopropane complexes reacted with aldehydes or ketones to give corresponding alcohols.

SYNTHESIS AND REACTIVITY OF BIS-(SILYLATED CYCLOPENTADIENYL) NIOBIUM  
COMPLEXES WITH CUMULENE LIGANDS.

A.Otero<sup>a</sup>, A.Antiñolo<sup>a</sup>, M.Fajardo<sup>a</sup>, F.Jalón<sup>a</sup>, C.López Mardomingo<sup>b</sup>, C.Sanz<sup>a</sup>, F.Florencio<sup>c</sup>  
and J.Sanz-Aparicio<sup>c</sup>.

<sup>a</sup>Departamento Química Inorgánica. <sup>b</sup>Departamento Química Orgánica. Universidad de  
Alcalá de Henares (Spain). <sup>c</sup>Departamento de Rayos X. Instituto Rocasolano. C.S.I.C.  
Madrid (Spain).

Metal-promoted activations on some cumulenes can simulate the metal-induced  
transformations on carbon dioxide<sup>1</sup>.

The synthesis and characterization of new "carbenoid like" niobium(III) sixteen  
electron species  $\text{Nb}(\eta^5\text{-C}_5\text{H}_3\text{RR}')_2\text{X}$ ,  $\text{R}=\text{H}$ ,  $\text{R}'=\text{SiMe}_3$ ,  $\text{X}=\text{Br}$ ;  $\text{R}=\text{R}'=\text{SiMe}_3$ ,  $\text{X}=\text{Cl}$  permits to de-  
termine the influence of electronic and steric effects in the relative stability  
of the compounds  $\text{Nb}(\eta^5\text{-C}_5\text{H}_3\text{RR}')_2\text{X}(\text{ZCY})$ ,  $\text{Z}=\text{Y}=\text{S}$ ;  $\text{Z}=\text{PhN}$ ,  $\text{Y}=\text{O}$  (or S) in comparison with  
the previously described<sup>2</sup> complexes with the cumulene coordinated on the  $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}$  unit.

The formation, properties and coordination modes of an extensive serie of ketene  
and keteneimine complexes with the fragments  $\text{Nb}(\eta^5\text{-C}_5\text{H}_3\text{RR}')_2\text{X}$ ,  $\text{R}=\text{H}$ ,  $\text{R}'=\text{SiMe}_3$ ,  $\text{X}=\text{Cl}$ ,  
 $\text{Br}$ ;  $\text{R}=\text{R}'=\text{SiMe}_3$ ,  $\text{X}=\text{Cl}$ , will also be deeply discussed because this type of complexes  
have been proposed as possible intermediacy in homogeneous carbon monoxide reduc-  
tion related to the Fischer-Tropsch process<sup>3</sup>.

These and other related reactions with other cumulene systems will be studied.

All the described complexes have been characterized by IR and NMR spectroscopy.  
Also for a keteneimine niobocene complex the X-ray crystal structure is being de-  
termined.

#### References

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2. A. Antiñolo, S. García-Lledó, J. Martínez de Ilarduya and A. Otero, *J. Organomet. Chem.*,  
(1987), 335, 85
3. D.A. Straus and R.H. Grubbs, *J. Am. Chem. Soc.*, (1982), 104, 5499

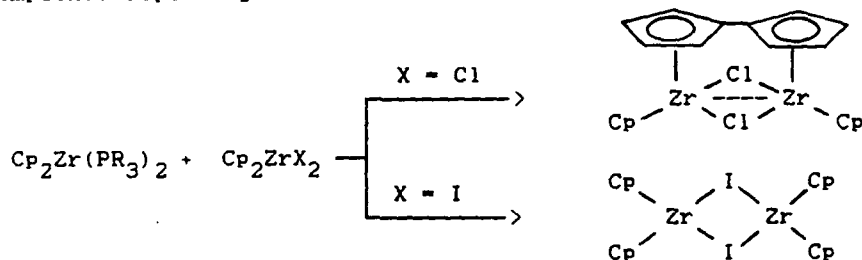
Synthesis of Diamagnetic and Dimeric Zirconium(III) and Hafnium(III) Compounds without Metal-Metal Bond

Sandro Gambarotta, Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16 9747AG Groningen, The Netherlands

Michael Y. Chiang, Chemistry Department, Columbia University, New York, N.Y. 10027, USA

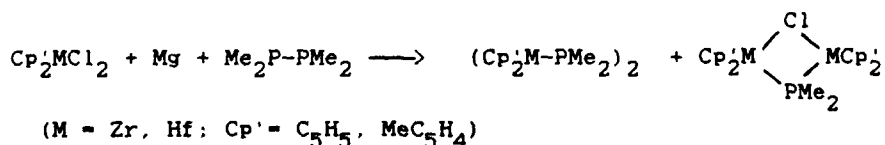
The formation of a Zr-Zr bond has been postulated to explain the generally observed diamagnetism of the dimeric Zr(III) species(1). However, there is in the literature a remarkable lack of structural reports(2).

Easy comproportionation reaction between  $\text{Cp}_2\text{ZrX}_2$  ( $\text{X} = \text{Cl}, \text{I}$ ) and  $\text{Cp}_2\text{Zr}(\text{PR}_3)_2$  leads to the formation of two different Zr(III) complexes depending on the nature of the halide.



The X-ray structure of both complexes showed a rather long intermetallic distance which, in the case of the diamagnetic  $(\text{Cp}_2\text{ZrI})_2$ , excluded the presence of any M-M bond.

The "in situ" generated " $\text{Cp}_2\text{Zr}$ ", reacts with  $\text{Me}_2\text{PPMe}_2$  originating two diamagnetic Zr(III) and Hf(III) complexes which can be easily isolated in pure form and characterized by X-ray analysis.



The value of the intermetallic distance shows that even in this case no M-M bond occurs as a common feature of these derivatives. The magnetic properties of these complexes will be discussed.

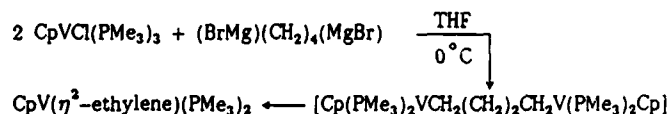
References:

- 1) Issleib, K. et al. Z. Naturforsch. (1966), 21b, 519
- 2) Lappert, M.F. Chemistry of organo zirconium and hafnium compounds Ellis Horwood 1984

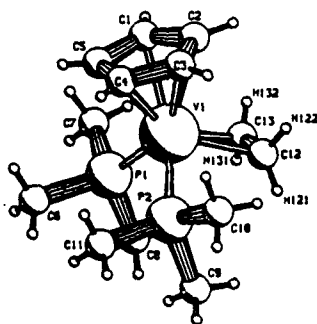
## AN ETHYLENE COMPLEX OF VANADIUM (I)

Bart Hessen, Auke Meetsma and Jan H. Teuben, Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.

The first ethylene complex of vanadium,  $\text{CpV}(\eta^2\text{-ethylene})(\text{PMe}_3)_2$ , was prepared by reaction of  $\text{CpVCl}(\text{PMe}_3)_2$  with 0.5 mol of 1,4-di(bromomagnesium)butane. The compound is paramagnetic. Its formation probably involves rearrangement of an intermediate 1,4-divanadabutane complex:



An X-ray structure determination showed that only a small amount of  $\pi$ -backdonation into the ethylene  $\bar{u}^*$ -orbital takes place ( $\text{C}-\text{C}$  (ethylene) = 1.365(5) Å).



The varied reactivity of  $\text{CpV}(\text{ethylene})(\text{PMe}_3)_2$  includes: (a) ligand exchange with (hard or soft) Lewis bases to yield new, CO-free  $\text{CpV(I)}$ -complexes, e.g.  $\text{CpV}(\text{PhC}\equiv\text{CPh})(\text{PMe}_3)_2$  and  $\text{CpV}(\text{bpy})\text{PMe}_3$ ; (b) insertion of  $\text{CO}_2$  into the metal-olefin bond; (c) oxidative addition to the low valent metal center; (d) catalytic dimerization of olefins.

## Transition Metal Siloxide Compounds

Alice C. Sullivan, Michael B. Hursthouse, M. Altaf Hossain, M. Mazid, Helen Blanchard, and Simon Bott. Department of Chemistry, Queen Mary College, University of London, Mile End Road, London E1 4NS.

A range of novel transition metal siloxide compounds having either unidentate or bidentate siloxide ligands are described. Some of the compounds along with features to be discussed are outlined below.

- (1)  $\{(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{O}\}_3\text{Cr}$  : Trigonal planar by Crystallography. First Cr(III) alkoxide with C.N. = 3<sup>1,2</sup>
- (2)  $\{(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{O}\}\text{TaCl}_4$  : Two isomers observed by <sup>1</sup>H N.M.R.<sup>1</sup>
- (3)  $\{(2\text{-Me-C}_6\text{H}_4)_3\text{SiO}\}\text{TaCl}_4\cdot\text{Et}_2\text{O}$  : Octahedral by Crystallography with the chlorides equatorial. Approx. linear Si-O-Ta ( $172.1(2)^\circ$ ) and short Ta-O ( $1.812(3)\text{\AA}$ )<sup>3</sup>
- (4)  $\{(2\text{-Me-C}_6\text{H}_4)_3\text{SiO}\}\text{TaMe}_3\text{Cl}$  : Trigonal bipyramidal by Crystallography.<sup>4</sup>
- (5) Formation and thermal decomposition of  $\{(2\text{-Me-C}_6\text{H}_4)_3\text{SiO}\}\text{TaMe}_4$ .
- (6)  $(\text{OPh}_2\text{SiOSiPh}_2\text{OSiPh}_2\text{O})_2\text{Ti}\cdot 2\text{pyridine}$  : cis-Octahedral by Crystallography. Formation from  $\text{Ph}_2\text{SiO}(\text{OLi})\text{SiPh}_2(\text{OLi})$  and  $\text{TiCl}_4$  involves interesting chain expansion.<sup>5</sup>

A full account of chemical features of these and other related compounds will be given.

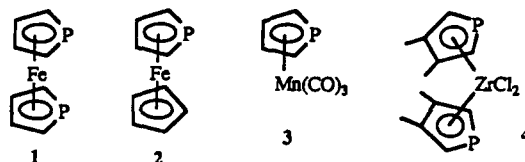
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4. Hursthouse M.B., Mazid M., and Sullivan A.C., unpublished work.
5. Hursthouse M.B., Hossain M.A., Mazid M., and Sullivan A.C., unpublished work.

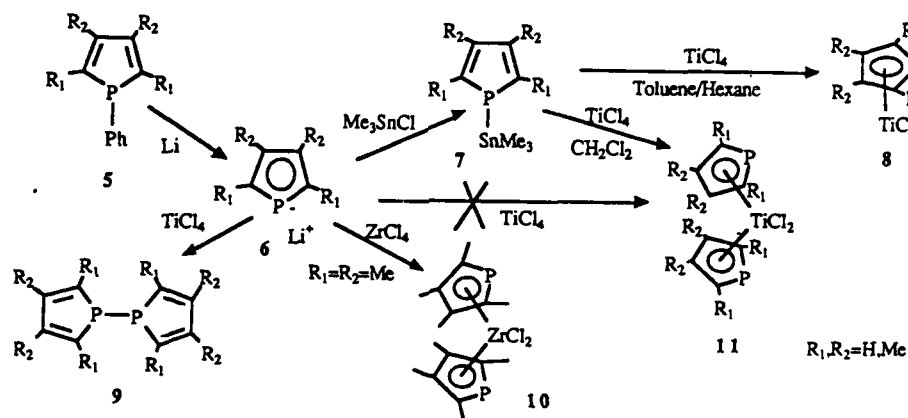
$\eta^5$ -PHOSPHOLYL COMPLEXES OF EARLY TRANSITION METALS.

François Nief and François Mathey, Laboratoire de Chimie du Phosphore et des Métaux de Transition, Ecole Polytechnique, 91128 Palaiseau Cedex, France.

Until now, most of the  $\eta^5$ -phospholyl (phosphacyclopentadienyl) complexes of transition metals belonged to the phospho- and diphosphaferrocene (1 and 2 respectively) or phosphacymantine (3) families<sup>1</sup>, with a few exceptions.



One of these exceptions is a diphosphazirconocene dichloride 4 which has been obtained<sup>2</sup> in modest yield and not completely characterized.



We have now been able to prepare the diphosphazirconocene dichloride 10 in good yield by reacting the new tetramethylphospholyl anion 6 ( $R_1=R_2=Me$ ) with  $ZrCl_4$ . Reaction of 6 with  $TiCl_4$  does not give the expected diphospha-titanocene dichloride but a biphospholyl 9 instead. However, this drawback was overcome by allowing a stannylphosphole 7 (easily obtained from 6) to react with  $TiCl_4$ . Depending on the solvent, a phospholyltitanium trichloride 8 or a bisphospholyltitanium dichloride 11 is obtained.

<sup>1</sup>F. Mathey, J. Fischer and J. H. Nelson, *Structure and Bonding* (Springer-Verlag, Berlin), 1983 **55**, 153

<sup>2</sup>P. Meunier and B. Gautheron, *J. Organomet. Chem.*, 1980 **193**, C13



### Activation of Alkynes with Ruthenium Complexes

P.H. Dixneuf

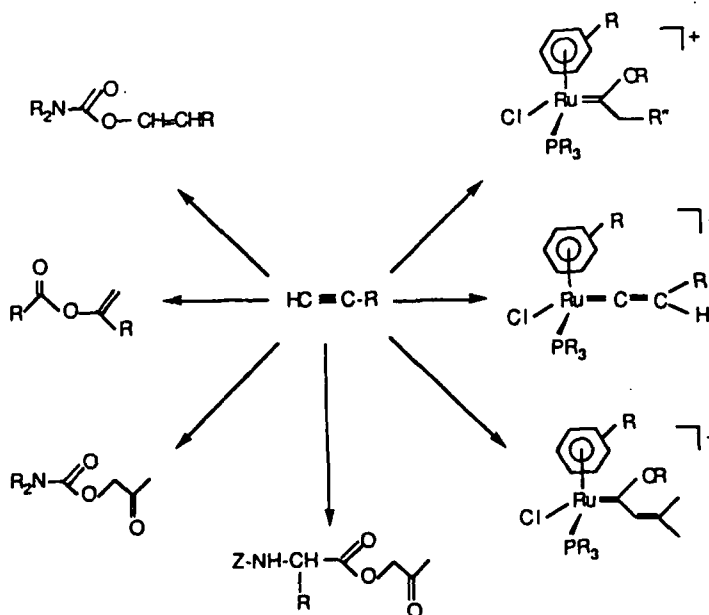
Université de Rennes, Campus de Beaulieu

35042 RENNES CEDEX (France)

Mononuclear ruthenium(II) complexes provide activation of alkynes towards both catalytic and stoichiometric additions.

They are catalyst precursors for the one-step synthesis of vinylcarbamates or enol esters directly from carbon dioxide or carboxylic acids. When propargyl alcohols are used this activation offers a route to  $\beta$ -oxopropyl carbamates and esters.

Activation of alkynes can be used for the access to new arene ruthenium-carbene complexes, via vinylidene intermediates, or to vinylcarbene derivatives via allenylidene intermediates.



## WATER SOLUBLE RHODIUM HYDROFORMYLATION SYSTEM

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Although a water soluble trisodium-phosphinetriyltri-m-benzenesulfonate  $[P(m-C_6H_4SO_3Na)_3]$  modified rhodium hydroformylation catalyst system has been successfully used in large scale production of n-butanal, no information was available on the structure of catalytic species under catalytic conditions.

We have found that  $Rh(CO)_2(acac)$  reacts with excess  $P(m-C_6H_4SO_3Na)_3$  ( $P/Rh=3.5$  or higher) in water under atmospheric pressure of carbon monoxide to give  $HRh(CO)[P(m-C_6H_4SO_3Na)_3]_3$  (1). The hydride ligand in 1 is formed via the water-gas shift reaction. NMR and IR spectroscopic data indicate a structure analogous to  $HRh(CO)(PPh_3)_3$  (2). The reaction of  $[Rh(CO)_2Cl]_2$  or  $Rh_4(CO)_{12}$  with  $P(m-C_6H_4SO_3Na)_3$  also yields 1. The formation of 1 was observed in the reaction of  $HRh(CO)(PPh_3)_3$  (2) with excess  $P(m-C_6H_4SO_3Na)_3$  as well.

Surprisingly, the  $HRh(CO)[P(m-C_6H_4SO_3Na)_3]_3$  (1)/3  $P(m-C_6H_4SO_3Na)_3$  system shows an extremely high stability under  $CO/H_2$ , the formation of new species could not be detected up to 200 bar of  $CO/H_2(1:1)$  by high pressure NMR. This sharply contrasts to the behavior of the  $HRh(CO)(PPh_3)_3$  (2)/3  $PPh_3$  system in organic media. Under the same conditions, 200 bar  $CO/H_2(1:1)$ , the only species in solution detectable by high pressure NMR is  $HRh(CO)_2(PPh_3)_2$ .

These results provide further evidence that the n/i ratio of aldehyde products is controlled either by the stereoselective coordination of the olefin to a coordinatively unsaturated  $\{HRh(CO)(phosphine)_2\}$  species and/or by the subsequent formation of the  $\{alkyl-Rh(CO)(phosphine)_2\}$  intermediate.

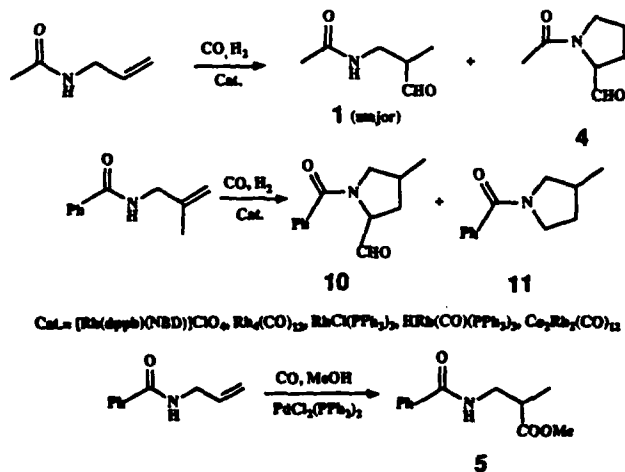
**Hydrocarbonylations of N-Allylamides. Novel Amide-directed  
Hydrocarbonylations and Double Carbonylation**

Iwao Ojima and Zhaoda Zhang

Department of Chemistry, State University of New York  
at Stony Brook, New York 11794, U.S.A.

The hydroformylation of N-allylacetamide is effected by the chelation of the amide moiety to rhodium catalysts giving iso-aldehyde (1) as a major product. Novel double carbonylation (a new type of amidocarbonylation) of N-allyl- and N-methallylamides giving 1-acyl-2-formylpyrrolidines (4, 10) is promoted by rhodium complexes. A Co-Rh mixed metal catalyst,  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ , gives 1 with a good regioselectivity and also promotes a new homologation-cyclization process to give 1-benzoyl-3-methylpyrrolidine (11) in one step with excellent selectivity. The  $\text{PdCl}_2(\text{PPh}_3)_2$ -catalyzed hydroesterification of N-allylbenzamide gives iso-ester (5) predominantly through a chelation-control.

Possible mechanisms for those new reactions are proposed.



## HYDROCARBONYLATION REACTIONS FOR KETONE SYNTHESIS

Giambattista Consiglio and Roger Schwab

Swiss Federal Institute of Technology (ETH), Department of Industrial and Engineering Chemistry, ETH Zentrum, CH-8092 Zürich

Despite its potential significance, the catalytic "oxo synthesis" of ketones has been very limited in scope until now [1]. In the last years large interest has been devoted to the copolymers of olefins (particularly of ethylene) and carbon monoxide [2]. Among the most active catalyst precursors for this copolymerization  $[Pd(CH_3CN)_4][BF_4]_2/PPh_3$  and  $Pd(OAc)_2/Dpp/Acid$  ( $Dpp=1,3$ -propanediylbis(diphenylphosphine); Acid=non-hydrohalogenic acid with a  $pK_a$  of less than 2) have been largely investigated [2,3]. The latter catalytic system (or the similar one containing the dpb ligand, where dpb is 1,4-butanediylbis(diphenylphosphine)) was reported to be active for the hydroformylation of 1-octene under about 100 bars of hydrogen and carbon monoxide and about 120 °C [4], the catalytic activity being much larger than that previously reported for the related systems based on  $Pd(PPh_3)_4/CF_3COOH$  or  $(PPh_3)_2Pd(C_6H_5)Br/AgPF_6$  [5]. In fact, by modifying the  $Pd(OAc)_2/CF_3COOH$  system with diphosphines such as dpp, dpb or even dpe we could carry out the hydroformylation of 1-pentene at 100 °C under 200 bars of hydrogen and carbon monoxide in equimolar ratio. However, when  $[Pd(CH_3CN)_4][BF_4]_2$  was used with the dpp ligand under the same reaction conditions, the most abundant hydrocarbonylation product (36 %) was a 4:1 mixture of undecan-6-one and 4-methyldecan-5-one. Partial hydroformylation (13 %) and hydrogenation (10 %) of the substrate takes also place. In the case of styrene as the substrate the reaction is much more selective, 1,5-diphenylpentan-3-one being recovered in 90 % yield. Yields for his system are thus much better than that recently reported for the formation of 4-oxo-heptandioate from methyl acrylate using  $Pd(OAc)_2/dpp/p$ .toluenesulphonic acid as the catalyst precursor [6].

References: 1) O. Roelen, Chem. Exp. Didakt. 3, 119 (1977). 2) A. Sen, Adv. Polym. Sci. 73/74, 125 (1986). 3) J.A.M. Van Broekhoven, E. Drent, Eur. Pat. Appl. 235,866 (1986) (C.A. 108, 38604 (1988)) and previous applications. 4) E. Drent, Eur. Pat. Appl. 220,767 (1985); C.A. 107, 39199 (1987). 5) J.J. Mrowca, U.S. Patent 3,876,672 (1972); C.A. 84, 30432 (1976). 6) E. Drent U.K. Pat. Appl. 2183631 (1985); C.A. 107, 153941 (1987).

DINUCLEAR RHODIUM COMPLEXES AS CATALYST PRECURSORS FOR THE HYDROFORMYLATION OF ALKENES.

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Juan Carlos Bayón and Julio Real, Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain.

In recent years dinuclear rhodium complexes have received considerable attention due to their catalytic activity in hydroformylation reactions. It has been shown that complexes of the types  $[\text{Rh}_2(\mu\text{-SR})_2(\text{CO})_2(\text{PR}_3)_2]^1$ ,  $[\text{Rh}_2(\mu\text{-azolate})_2(\text{COD})_2]$  plus  $\text{PR}_3$  ligands and related complexes<sup>2-4</sup>, behave as active catalyst in alkene hydroformylation, even in mild conditions.

A potential advantage of these species with respect to other catalysts is the possibility of introducing changes in the bridging ligands.

The present investigation was undertaken in order to explore the use of anionic and zwitterionic amino-thiols as bridging ligands to produce new complexes of rhodium(I). Neutral and cationic dinuclear complexes of formulation  $[\text{Rh}_2(\text{COD})_2(\text{S}(\text{CH}_2)_3\text{NMe}_2)_2]$  and  $[\text{Rh}_2(\text{COD})_2(\text{S}(\text{CH}_2)_3\text{NMe}_2\text{Bz})_2](\text{PF}_6)_2$  and related carbonyl complexes have been prepared and characterized by elemental analyses, infrared spectra,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

The systems formed by adding phosphine or phosphite ligands ( $\text{PR}_3/\text{Rh} = 1/1$ ) to the dinuclear complexes are catalysts precursors in hydroformylation of 1-heptene under mild conditions (5 bar, 80°C).

The best conversion from 1-heptene to aldehydes was achieved when  $\text{PR}_3 = \text{PPh}_3$  (90%) and the best selectivity (n-octanal/2-methylheptanal = 3/1) when  $\text{PR}_3 = \text{P}(\text{OMe})_3$ .

References: 1) Ph. Kalck, J. M. Frances, P. Pfister, T. Southern and A. Thorez J. Chem. Soc. Chem. Commun., 1983, 510. 2) Ph. Kalck, A. Thorez, M. T. Pinillos, L. A. Oro, J. Mol. Cat., **31**, 1985, 311. 3) C. Claver, Ph. Kalck, L. A. Oro, M. A. Pinillos and C. Tejel, J. M. Cat. (in press) 4) C. Claver, Ph. Kalck, M. Ridmy, A. Thorez, L. A. Oro, M. T. Pinillos, M. C. Apreda, F. H. Cano and C. Foces-Foces, J. Chem. Dalton Trans (in press).

OXIDATIVELY INDUCED MIGRATION OF HYDROGEN FROM METAL TO ALKENE.  
HIGHLY REACTIVE RHODIUM SYSTEMS FOR HYDROGENATION AND HYDROFORMY-  
LATION OF ALKENES AND ALKYNES.

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Piero Frediani, Dipartimento di Chimica Organica, Università di Firenze, Via G. Capponi 7, I-50121 Firenze, Italy

The formation of alkyl complexes via migratory insertion of alkene into a transition metal-hydrogen bond has long been a goal in organometallic chemistry, in large part because of the importance of the reaction in catalytic hydrogenation of alkenes. Generally, such a migratory step is accomplished by ligand addition to hydride(alkene) complexes.

We now wish to report an alternative pathway by which the hydride (alkene)  $\longrightarrow$  alkyl migration takes place. The  $[(\text{triphos})\text{RhH}(\pi\text{-dialkyl fumarate})]$  complex, (1),  $[\text{triphos} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3]$  converts to the stable  $[(\text{triphos})\text{Rh}(\sigma\text{-alkyl})]^2+$  derivative upon two-electron chemical or electrochemical oxidation. The process is reversible, i.e. the two-electron reduction restores the starting hydride( $\pi$ -fumarate) complex via Rh(II)-alkyl and Rh(I)-alkyl intermediates.

Results on the hydrogenation and hydroformylation of alkenes and alkynes using 1 as catalyst precursor are discussed.

BIMETALLIC ACTIVATION IN HOMOGENEOUS CATALYSIS :  
PALLADIUM CATALYZED MONO AND DOUBLE CARBONYLATION OF CHLOROARENE CHROMIUM  
TRICARBONYL COMPLEXES

Robert MUTIN, Christine LUCAS, Jean THIVOLLE-CAZAT, Fabienne DANY,  
Véronique DUFAUD and Jean Marie BASSET

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The palladium catalyzed carbonylation of aryl bromide or iodide to aromatic carboxylic acids, esters, amides, aldehydes or to aromatic  $\alpha$ -keto amides,  $\alpha$ -keto esters and  $\alpha$ -keto acids is now well documented. However and so far, there is no reliable example of carbonylation of chlorobenzene leading to the same products. The difficulty to carry out carbonylation of chloroaromatic compounds is probably due to the high temperature required for the oxidative addition of the C-Cl bond onto zerovalent palladium complexes.

We report here that the palladium catalyzed carbonylation of chloroarene chromium tricarbonyl complexes, can lead to the corresponding esters, aldehydes, amides or  $\alpha$ -keto amides. In the case of methoxy carbonylation, methyl-benzoate chromium tricarbonyl can be obtained at 100°C, with a selectivity of 95%. This result strongly suggests that the whole catalytic cycle of carbonylation proceeds via bimetallic intermediates where chromium and palladium are simultaneously bonded to the same organic substrate. Consequently, it is suggested that the  $\text{Cr}(\text{CO})_3$  moiety favors the oxidative addition of the arene-Cl bond to zerovalent palladium and makes it possible a subsequent catalytic cycle of carbonylation.

Acknowledgements : The authors wish to thank R.P. Industries for financial support.

## ALKYLALKOXYCARBONYLTETRACARBONYLIRON COMPLEXES

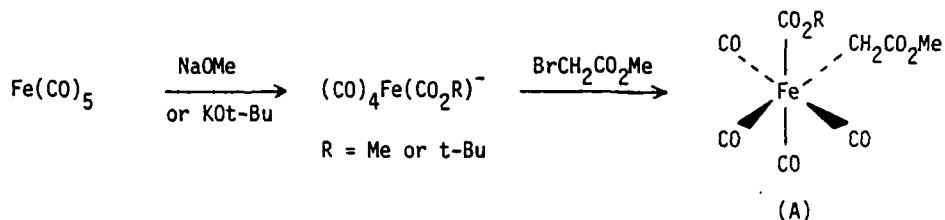
## ISOLATED INTERMEDIATES IN THE CATALYTIC CARBONYLATION OF ORGANIC HALIDES

Pascale Laurent, Sylviane Sabo-Etienne and Hervé des Abbayes

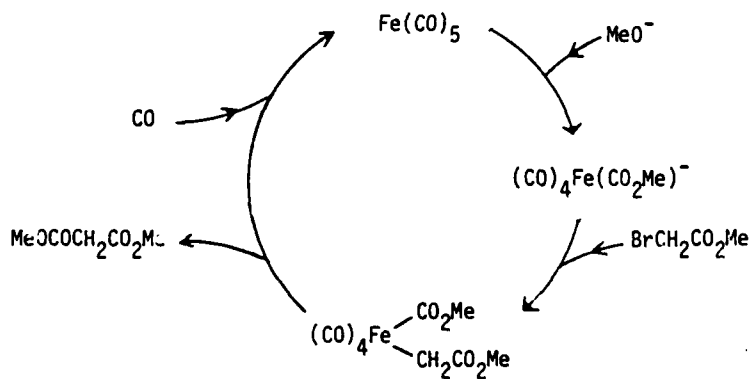
Laboratoire de Chimie Organique des Eléments de Transition, UA CNRS 322

Université de Bretagne Occidentale, 29287 Brest-Cédex FRANCE

Alkylalkoxycarbonyl complexes are believed to be intermediates in important catalytic reactions. We report here the synthesis and characterization of  $(\text{CO})_4\text{Fe}(\text{CH}_2\text{CO}_2\text{Me})(\text{CO}_2\text{R})$  complexes and provide direct evidence for their involvement in the catalytic cycle of carbonylation of organic halide into ester.



For R = Me, the complex (A) decomposes above 20°C under a CO atmosphere to yield  $\text{Fe}(\text{CO})_5$  and dimethylmalonate. (A) can be considered as an intermediate in the catalytic carbonylation of  $\text{BrCH}_2\text{CO}_2\text{Me}$  into ester, according to the following cycle :



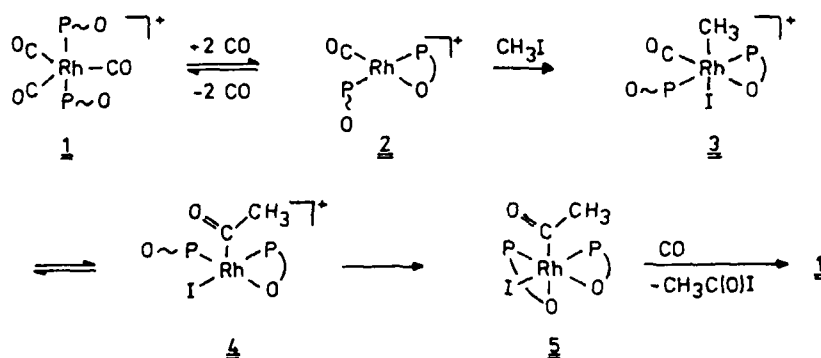


ETHER-PHOSPHINES AS CONTROLLING LIGANDS IN  
THE HYDROCARBONYLATION OF METHANOL

Ekkehard Lindner, Erhard Glaser, Uwe Schober, and Anselm Sickinger,  
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Tetrahedrally coordinated cobalt(I) complexes of the type  $\text{ICo}(\text{P}\sim\text{O})(\text{P}\sim\text{O})(\text{P}\sim\text{O})$  ( $\text{P}\sim\text{O}$ : P-coordinated;  $\text{P}\sim\text{O}$ : O, P-coordinated), containing specifically conceived ether-phosphines as controlling ligands, are precursors in the catalytic cycle of the hydrocarbonylation of methanol. They are obtained by reaction of  $\text{I}_2\text{Co}(\text{P}\sim\text{O})_2$  with  $\text{K}[\text{HB}(\text{sec-C}_4\text{H}_9)_3]^{1)}$ . Methanol conversions and selectivities to acetaldehyde have attained more than 80%.

(Ether-phosphine)-rhodium complexes are useful as model compounds in the carbonylation of methanol<sup>2)</sup>. CO elimination from 1 yields



2. With rapid methyl migration via 3 and 4 oxidative addition of  $\text{CH}_3\text{I}$  to 2 affords the acyl complex 5. Heating of 5 in the presence of CO results in the reductive elimination of  $\text{CH}_3\text{C(O)I}$ . The formation of the individual complexes is promoted by the "opening and closing mechanism" of (ether-phosphine) ligands.

1) E. Lindner, U. Schober, E. Glaser, H. Norz, and P. Wegner, *Z. Naturforsch.* **42b**, 1527 (1987).

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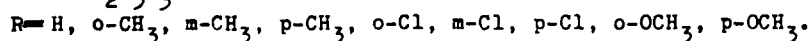
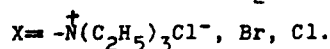
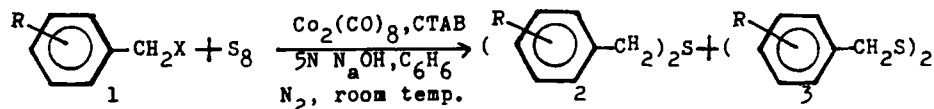
SYNTHESIS OF SULFIDES BY THE  $\text{Co}_2(\text{CO})_8$  AND  
PHASE TRANSFER CATALYZED REACTIONS OF BENZYL CHLORIDES

Jinxian Wang

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Since the first publication on organometallic phase transfer catalysis<sup>1</sup>, the field has developed sufficiently rapidly to justify an account at this time. Recent investigations have demonstrated that phase transfer catalysis is an exceedingly useful technique in organometallic chemistry. Several good reviews was published by Cassar<sup>2</sup> and Alper<sup>3</sup>.

Sulfides are an important organic compounds. The preparation of sulfides by reaction of halides with  $\text{Na}_2\text{S}$  are well known in synthetic organic chemistry. We now report the synthesis of dibenzylsulfides and dibenzyl disulfides by the  $\text{Co}_2(\text{CO})_8$  and phase transfer catalyzed reactions of benzyl chlorides with  $\text{S}_8$ .



Sixteen sulfides were prepared by the  $\text{Co}_2(\text{CO})_8$  and phase transfer catalyzed reactions of benzyl chlorides. The total yield is above 90%. Their structures have been proved by IR, MS, NMR and elemental analysis. The reaction mechanism is briefly discussed.

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- 4) Jinxian Wang,H.Alper, J.Org.Chem., 51, 273(1986).

Organosilicon Reagents in Organic Synthesis

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Haifa, Israel

## CYCLOMETALLATION CHEMISTRY OF METHYL-SUBSTITUTED TRIPHENYLPHOSPHINES

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It has now been well established that large tertiary phosphine ligands can promote cyclopalladation and/or cycloplatination reactions. Our presentation will quickly review the known trends in this chemistry and then focus on the closely related series of methyl-substituted triphenylphosphines,  $P(C_6H_5-n(CH_3)_n)_3$ , ( $n=0-4$ ). Cyclometallation is not observed in all cases but depends on the metal and its environment as well as the reaction conditions employed. As expected, the relative bulk of the phosphine is very important but the overall ligand electronic properties also prove to be important. Comparisons are made to parallel reactions of bulky trialkylphosphine ligands and all the factors which facilitate internal metallation are summarized so as to suggest a more definite description for the intimate mechanism(s) for metal-carbon bond formation via cyclometallation.

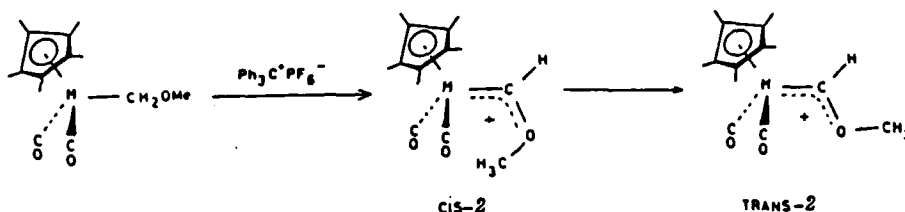
STEREO- AND CHEMO-SELECTIVE  $\alpha$ -HYDRIDE ABSTRACTION FROM  
TRANSITION METAL ALKYL COMPLEXES

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The alkyl complexes  $M(C_5Me_5)(L^1)(L^2)(CH_2XR)$  -  $M = Fe, Ru$ ,  $X = O, S$ - provide an attractive chemistry in connection with the access to electrophilic carbene species. Their reactivity - the nature of the leaving group ( $H^-$  vs.  $CH_3O^-$  or  $S$ -adducts), the stereoselectivity of the  $\alpha$ -hydride abstraction (geometric isomers) - are both controlled by the ancillary ligands at the metal center and by the nature of the abstracting reagent (the trityl cation and the in situ generated methylene complex  $[Fe=CH_2]^+$  have been employed).

Complex **1** ( $L^1 = L^2 = CO$ ,  $XR = OCH_3$ ) undergoes an  $\alpha$ -hydride abstraction with  $Ph_3C^+PF_6^-$  affording specifically the kinetic cis isomer of **2** which then isomerizes into the thermodynamic trans form.



Such a behavior suggests an initial interaction of the trityl cation with the oxygen atom of the methoxy group of **1**. This assumption is supported by the change of the chemoselectivity either observed upon substitution of a carbonyl ligand by a phosphine or in the case of the parent sulfur-containing complex which leads to the formation of stable adducts. The electrophilic properties of the carbene complexes have been investigated.

C-H BOND ACTIVATION: THE EIGHTEEN ELECTRON RULE AND THE  
GENERATION OF CATALYSTS

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Bis(arene)metal sandwiches are usually stable if they do not exceed an 18-e<sup>-</sup> count, the bis(hexamethylbenzene) d<sup>7</sup>-d<sup>8</sup> group VIII metal complexes being only apparent exceptions because distortions either alterate the energy levels, and thus the basis of the 18-e<sup>-</sup> rule itself, or reduce the hapticity of one of the ligands.

In group VI bis(arene) sandwiches, a ligand is labilized by contact with potassium metal.<sup>1</sup> We report here that such a labilization can generate catalytic systems.

A mixture of 1,4-cyclohexadiene (5.3 mmol), di(benzene)molybdenum(0) (0.24 mmol) and potassium sand (0.59 mmol) in 1,2-dimethoxyethane (25 cm<sup>3</sup>) was stirred overnight at room temperature (15° C). This resulted in the total conversion of the diolefin to benzene and dihydrogen (G.C.). Preliminary results show that also chromium and iron arene complexes are active in the same reaction.

Discussions with Prof. F. Calderazzo and Prof. G. Fachinetti were very helpful. M.P.I. (ministero della pubblica istruzione), Rome, is gratefully acknowledged for financial support.

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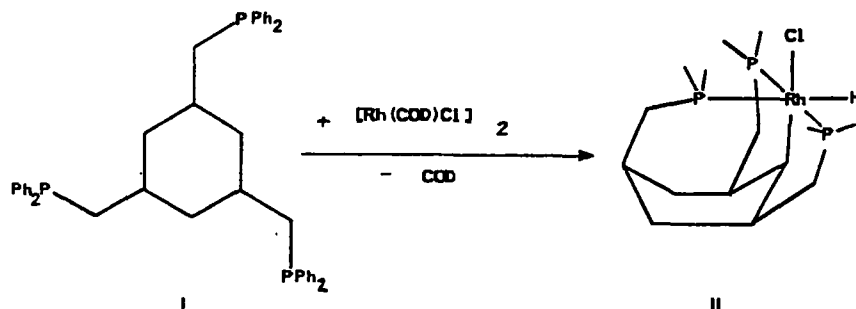
1) M. L. H. Green, G. Parkin, J. Chem. Soc., Chem. Comm., 1985, 771.

THE METALATION OF C-H BONDS BY RHODIUM.  
 CIS,CIS-1,3,5-TRIS(DIPHENYLPHOSPHINOMETHYL)-  
 CYCLOHEXANE

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The novel tridentate phosphine cis,cis-1,3,5-Tris(diphenylphosphinomethyl)-  
 cyclohexane (I) has been synthesized.



Treatment with  $[\text{Rh}(\text{COD})\text{Cl}]_2$  in toluene at elevated temperatures gives a yellow solid (II). Compound II was characterized by  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR. Spectroscopy of the intramolecular C-H metalated product. Broad NMR lineshapes suggest that intramolecular exchange processes occur between the metal and the cyclohexane frame. Treatment with carbon monoxide gives different complexes with the cleavage of the Rh-C bond. Carbon-hydrogen metalation, exchange processes and reaction with carbon monoxide will be discussed.

## ALLYLSTANNATION IN AQUEOUS MEDIUM

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Allyl-, allenyl-, and propargyl-stannation of carbonyl compounds have recently been developed using allyl-, allenyl- and propargyl-tin chlorides (1-3). The procedure is based on:  
$$\text{Bu}_2\text{RSnCl} + \text{R}'\text{COR}'' + 1/2\text{H}_2\text{O} \rightarrow \text{R}(\text{HO})\text{CR}'\text{R}'' + 1/2(\text{Bu}_2\text{SnCl})_2\text{O},$$
where R= allyl, allyllike, allenyl, or propargyl;  
R' = H or alkyl; R'' = alkyl group.

Organotin substrates having allyl, crotyl, 1-methylallyl, cyclohex-2-enyl, and cinnamyl groups easily react in the presence of water with carbonyl compounds such as aldehydes, dialdehydes, ketones and acetals to give homoallyl alcohols(3).

The stereochemical course of some of these reactions has been evaluated by changing the experimental conditions.

Work supported by C.N.R. (Roma).

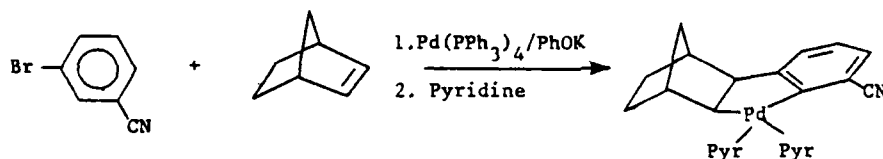
- (1) A. Boaretto, D. Marton, G. Tagliavini and A. Gambaro, J. Organometal. Chem., 286 (1985) 9.
- (2) A. Boaretto, D. Marton and G. Tagliavini, J. Organometal. Chem., 297 (1985) 149.
- (3) D. Furlani, D. Marton, G. Tagliavini and M. Zordan, J. Organometal. Chem., 341 (1988) 345.



## DIRECT SYNTHESIS OF A NEW ALKYLAROMATIC PALLADACYCLE.

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In the course of studies aimed at isolating intermediates of palladium-catalyzed C-C bond formation reactions [1], a new palladacycle has been obtained as a whitish solid powder from the reaction of *m*-bromobenzonitrile with bicyclo [2.2.1] hept-2-ene in anisole at 105° C in the presence of  $\text{Pd}(\text{PPh}_3)_4$  and potassium phenoxide. The complex is insoluble in non coordinating solvents. On addition of pyridine it goes into solution while preserving its metallacyclic structure, as shown by n.m.r. evidence:



The composition and structure of the complex clearly result from decomposition with  $\text{NaBD}_4$ , which gives the expected dideuterated cyanophenylbicycloheptane.

To our knowledge this is the first direct preparation of a palladacycle by one-pot oxidative addition, insertion and aromatic substitution in sequence.

Work supported by Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione.

1. M. Catellani and G.P. Chiusoli, J. Organomet. Chem., in press.

## A STEREOSELECTIVE SYNTHESIS OF ALLYLIC ALCOHOLS

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The reaction of vinyl epoxide with Grignard reagents and methyl-lithium was reported to give the mixture of 1,2- and 1,4-adducts and with organocopper reagents to give 1,4-adducts of E-configuration. Although it was claimed that the reaction of phenyllithium with isoprene epoxide gave a 1,4-adduct of Z-configuration as a major product, 1,2-adduct was always accompanied to some extent when the reaction was reinvestigated.

It was found that alkyllithiums react with vinyl epoxide regioselectively and stereoselectively to give 1,4-adducts. The major isomer was shown to have Z-configuration on the basis of <sup>1</sup>H-NOE, <sup>13</sup>C- and <sup>1</sup>H-NMR. The predominance of Z-isomer was improved when the reaction was conducted in the presence of a base such as tertiary amine or lithium alkoxide. The results are summarized in Table. This unexpected reactivity is limited to alkyllithiums and the organolithium compounds other than alkyllithium such as allyllithium, benzylithium, 3-pyrridylithium and 2-phenylvinylithium gave only 1,2-adducts.

The present method was successfully applied to a stereoselective synthesis of α-santalol, which is one of the main constituents in East Indian sandalwood oil.

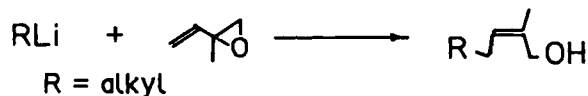


Table.

R	Base	Temp(°C)	Solvent	Yd(%)	Z/E
n-C <sub>4</sub> H <sub>9</sub>	none	0	Hexane	76	88/12
	TMEDA	0	"	68	96/4
"	n-C <sub>4</sub> H <sub>9</sub> OLi	0	"	73	97/3
sec-C <sub>4</sub> H <sub>9</sub>	none	0	"	63	86/14
n-C <sub>8</sub> H <sub>17</sub>	TMEDA	-20	"	55	96/4
cyclo-C <sub>3</sub> H <sub>5</sub>	none	-30	Et <sub>2</sub> O	77	82/18
cyclo-C <sub>6</sub> H <sub>11</sub>	none	"	"	55	89/11
PhCH <sub>2</sub> CH <sub>2</sub>	none	"	"	70	79/21
	TMEDA	-20	"	59	98/2

## INTRAMOLECULAR ADDITION REACTIONS OF IRON CARBENE COMPLEXES

Paul Helquist, Christopher Knors, Shi-Kai Zhao, Pascale Seutet, and Matthew Mattson., University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

We have obtained several examples of carbene complexes of the general structure  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{L})\text{Fe}=\text{CR}^1\text{R}^2]^+$  (L = CO, phosphite, or phosphine). These species may be generated from the corresponding  $\alpha$ -(alkylthio)alkyl-, alkenyl-, or acyliron complexes. Some of the carbene complexes are quite stable and have been characterized spectroscopically and by x-ray diffraction. Furthermore, many of these compounds show quite useful reactivity such as addition to alkenes to give cyclopropanes.

Most recently, we have been placing emphasis upon the uses of these complexes in the synthesis of polycyclic organic compounds proceeding through intramolecular additions of the carbene ligands to alkenes. Complex fused-ring cyclopropane derivatives are normally obtained, but we have also been studying the formation of five-membered rings. Current studies are being directed toward applications of these reactions in very direct syntheses of a variety of naturally occurring compounds. These syntheses have in turn required us to develop methods for the incorporation of the carbene complexes into organic substrates that serve as precursors of the natural products.

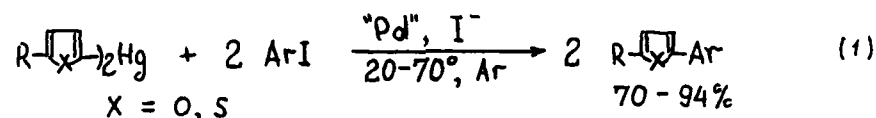
## Literature References:

- K. A. M. Kremer and P. Helquist, J. Organomet. Chem. **1985**, 285, 231 (1985).  
R. S. Iyer, G.-H. Kuo, and P. Helquist, J. Org. Chem. **1985**, 50, 5898.  
E. J. O'Connor, S. Brandt, and P. Helquist, J. Am. Chem. Soc. **1987**, 109, 3739.  
C. Knors, G.-H. Kuo, J. W. Lauher, C. Eigenbrot, and P. Helquist, Organometallics **1987**, 6, 988.

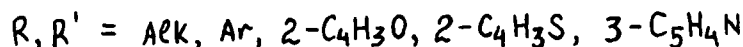
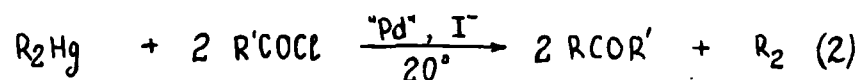
PALLADIUM-CATALYZED CROSS-COUPLING, ACYL-DEMETALLATION AND  
CARBONYLATION REACTIONS OF ORGANOMERCURIALS

Prakash More, Nikolai Bumagin, Irina Beletskaya  
Moscow State University, Moscow, USSR.

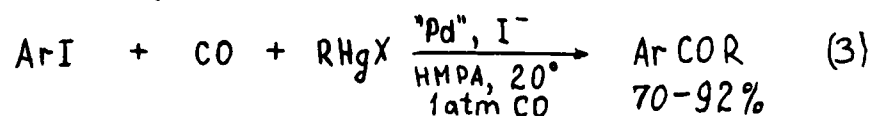
The palladium-catalyzed cross-coupling reactions of organomercurials with organic halides provide a novel and convenient method for the synthesis of arylated heterocyclic compounds. The reaction proceeds in the presence of iodide ion and oxygen-free atmosphere in dimethyl formamide to give a high yield of cross-coupling product (eq. 1).



The palladium-catalyzed acyl-demetalation of organomercurials is a mild, selective and general method for the synthesis of unsymmetrical ketones (eq. 2). The reaction proceeds at room temperature in acetone and in the presence of iodide ion to give high yields of unsymmetrical ketones (79-85%) along with the formation of homo-coupling product (~15%). The yield of unsymmetrical ketone can be increased by carrying out the reaction in vacuum.



Carbonylation of  $\text{ArI-RHgX}$  system in the presence of palladium catalyst and iodide ion is another route to get high yields of unsymmetrical ketones (eq. 3). The highest reaction rate and selectivity was found in HMPA and in the presence of ligandless palladium catalyst.



**POSTER SESSION**

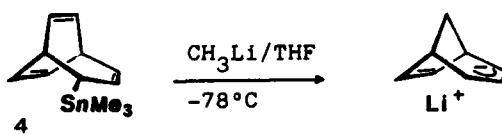
LITHIUM, POTASSIUM, AND STANNYL DERIVATIVES  
OF BI- AND TRICYCLIC CARBANIONS

J. Blümel, N. Hertkorn, F. H. Köhler, Anorganisch-chemisches Institut der TU München, Lichtenbergstr. 4, 8046 Garching, W-Germany.

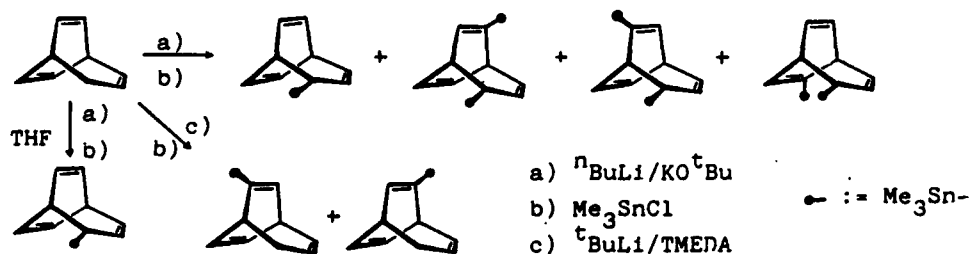
Metal derivatives of perturbed cyclopentadienyl anions represent a fascinating topic in Organometallic Chemistry. A special kind of perturbation is the twofold interruption of the originally cyclic  $\pi$ -system by  $sp^3$ -C-atoms as in 1, 2, and 3.



We have obtained the lithium derivatives of 1, 2 and 3 according to the example given in the following equation.



A simple and fast access to the stannyl derivatives like 4 is provided by direct metalation of the olefins and reaction with trimethyltinchloride or by stannyl halogen exchange. In addition, a variety of stannyl compounds can be obtained selectively depending on the metalation conditions, e. g.:



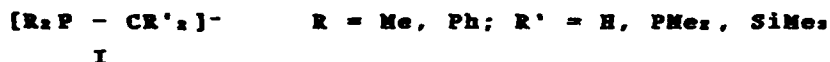
All stannylated derivatives are characterized by their NMR spectra. The data obtained therefrom lead to useful trends for the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  signal shifts and for the nuclear coupling constants  $n_J(^{117/119}\text{Sn}-^{13}\text{C})$  and  $n_J(^{117/9}\text{Sn}-^{119}\text{Sn})$ .

REMARKABLE STRUCTURAL ANALOGIES BETWEEN  $\text{Li}^+$  AND  $\text{Cp}_2\text{ZrCl}^+$  COMPLEXES.

Gerhard Müller, Jürgen Riede, Brigitte Huber, Gabi Reber, Hans Heinz Karsch, Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstr. 4, D-8046 Garching, FRG.

Unexpected structural analogies between organometallic complexes of  $\text{Li}^+$  and  $\text{Cp}_2\text{MCl}(\text{d}^0)$  fragments were first predicted by Schleyer [1]. These should be due to electronic similarities of the metal fragments.

In a variety of molecular structures of *phosphinomethanide* complexes of  $(\text{TMEDA})\text{Li}^+$  and  $\text{Cp}_2\text{ZrCl}^+$  [2] some remarkable structural analogies may actually be substantiated. These are not limited to virtually identical Li-P/C and Zr-P/C bond lengths, but are also evident in similar coordination modes of the ambident *phosphinomethanide* ligands I (monodentate via P or C; bidentate under formation of a three-membered ring).



Surprisingly, at both metal centers the coordination mode of the ligands is less influenced by the P substituents R, but rather by those at the carbanionoid C atoms ( $\text{R}'$ ). Bidentate, chelating coordination is favored by +I substituents, e.g.,  $-\text{PMe}_2$  or  $-\text{SiMe}_3$  which induce higher coordination numbers at the central metal atoms despite their greater steric bulk.

Similarities with, and differences to, theoretical studies on Li-phosphinomethanides (by P.v.R. Schleyer et al.) and  $\text{Cp}_2\text{ZrCl}^+$ -phosphinomethanides (by P. Hofmann) are discussed.

- [1] A.J. Kos, E.D. Jemmis, P.v.R. Schleyer, R. Gleiter, U. Fischbach, J. Pople, J. Am. Chem. Soc. 103 (1981) 4996.
- [2] H.H. Karsch, B. Deubelly, G. Müller, J. Organometal. Chem., in the press; H.H. Karsch, B. Deubelly, J. Hoffmann, U. Pieper, G. Müller, J. Am. Chem. Soc., in the press.

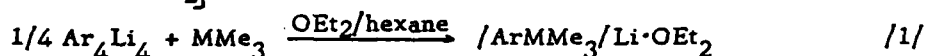
THE DYNAMIC PROPERTIES OF THE ARYLGANOLITHIUM "ATE"  
COMPLEXES  $/ArMR_3/Li \cdot D/$   $M=B, Al/$  INVESTIGATED BY MEANS OF  
MULTINUCLEAR H-1, C-13, Li-7, B-11, Al-27 DYNAMIC NMR  
SPECTROSCOPY

E. Kalbarczyk-Bidelska, S. Pasynkiewicz, Warsaw Technical University, .  
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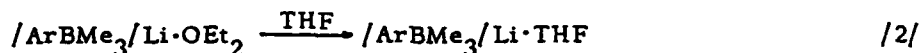
G. van Koten, University of Utrecht, 3508 TB Utrecht /The Netherlands/

J.M. Ernsting, University of Amsterdam, 1018 Amsterdam /The Netherlands/

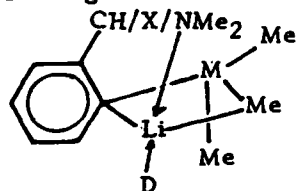
The model  $/ArMMe_3/Li \cdot D/$  [I  $Ar=Ar^1=2-C_6H_4CH_2NMe_2$ ,  $M=B$ ,  $D=-OEt_2$ ; II  $Ar=Ar^2=2-C_6H_4-S-CHMeNMe_2$ ,  $M=B$ ,  $D=OEt_2$ ; III  $Ar=Ar^2$ ,  $M=Al$ ,  $D=OEt_2$ ] were synthesized in the complexation reaction 1.



The complexes IV  $Ar=Ar^1$ ,  $M=B$ ,  $D=THF$ , V  $Ar=Ar^2$ ,  $M=B$ ,  $D=nTHF$  were synthesized via the donor exchange reaction 2.



The following structure has been established on the basis of molecular weight determinations and NMR spectroscopy:



	Li-7	B-11	Li-7	Al-27
I	-0.49	-17.2	III	-0.17
II	-0.72	-17.17		150.8
IV	-0.56	-17.72		
V	-0.98	-17.41		

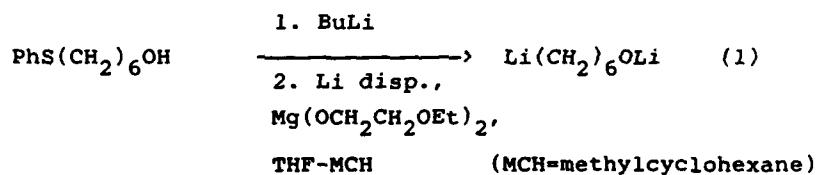
The flexibility of the molecules has been detected in polar and non-polar solvents. The intramolecular two steps "rotation" of the aryl ring was found in  $D_8$ -toluene solution for the I-IV complexes. The intramolecular processes, involving carbon-lithium bond, in  $OEt_2$  solution at low temperature and in THF solution at raised temperatures were established.



METAL ALKOXIDE MODIFIED ORGANOMETALLIC REACTIONS. DIRECT SYNTHESIS  
OF LITHIOOXYALKYL- AND ARYLITHIUM COMPOUNDS

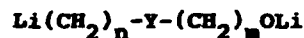
C.G.Screttas ,I.D.Kostas and C.S.Salteris, Institute of Organic  
Chemistry The National Hellenic Research Foundation Athens 116 35  
Greece

Attempts to synthesize  $\text{LiO}(\text{CH}_2)_6\text{Li}$  according to the conventional method from  $\text{HO}(\text{CH}_2)_6\text{Br}$  led to extensive Wurtz coupling. Similar results were obtained by employing lithium naphthalene radical anion in place of lithium metal. 6-Lithiooxyhexyllithium was prepared in fair yields according to eq. (1).

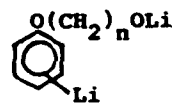


The organometallic product was characterized by carbonation and by conversion to  $\text{Hg}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_2$ . The function of the alkoxide is to stabilize the organometallic reagent with respect to THF-cleaving reaction, so that solutions of the reagent can be stored at room temperature for 48 hours or longer.

The method has been extended to the preparation of the lithio-oxy- organolithiums of the general types 1 and 2 .



1



2

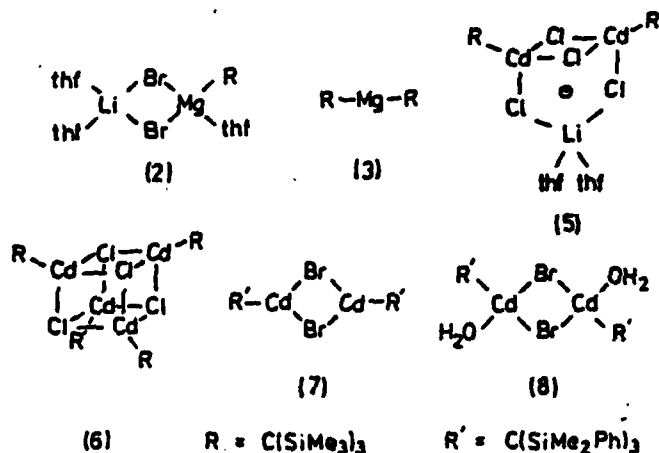
STERICALLY HINDERED ORGANOMETALLIC COMPOUNDS  
OF GROUPS 2 AND 12

Salih S. Al-Juaid, Colin Eaborn, Peter B. Hitchcock,  
Catherine A. McGeary, J. David Smith and Kayumars Tavakkoli. School  
of Chemistry and Molecular Sciences, University of Sussex, Brighton  
BN1 9QJ, UK.

The compound  $RLi$  ( $R = C(SiMe_3)_3$ ) (1) reacts with anhydrous magnesium(II) bromide to give the bridged lithium-magnesium complex (2) (thf = tetrahydrofuran) which on heating gives the dialkyl  $MgR_2$  (3), with the same structure as the compounds  $R_2M$  ( $M = Zn, Cd, Hg$ , or  $Mn$ ) described earlier.

With cadmium(II) chloride, (1) gives  $Li(thf)_2CdRCl_2$  (4) which has an ionic structure with the unusual dicadmiate anion (5). On heating (4) gives  $RCdCl$  which has the tetrameric cubane structure (6). In contrast, the compound  $R'CdBr$  ( $R' = C(SiMe_2Ph)_3$ ) (7), is dimeric in the solid: on recrystallisation from moist thf, the hydrate (8) is formed.

The mercury compound  $R'HgCl$  reacts with organolithium or Grignard reagents to give the unsymmetrical compounds  $R'HgR'$  ( $R' = Me, Bu, Ph, CH_2Ph$  or  $C(SiMe_3)_3$ ) which are remarkably stable thermally. No decomposition of  $(Me_2PhSi)_3CHgCH_2Ph$  was detected at 230 °C whereas  $Hg(CH_2Ph)_2$  was completely decomposed at 150-170 °C. If, as is generally supposed, the rate determining step in the decomposition of dibenzyl mercury is homolytic cleavage of the  $Hg-C$  bond, it is not clear why the large alkyl group in the unsymmetrical  $R'HgCH_2Ph$  should make this cleavage so difficult.

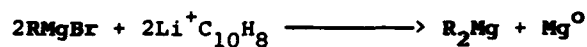


M.H. Buttrus, C. Eaborn, M.H.A. El-Kheli, P.B. Hitchcock,  
J.D. Smith, A.C. Sullivan, and T. Tavakkoli, J. Chem. Soc. Dalton  
Trans. 1988, 381, and unpublished results.

STOICHEIOMETRY OF REACTION BETWEEN RADICAL ANIONS AND METAL  
COMPOUNDS

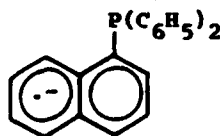
Constantinos G. Screttas and Maria Micha-Screttas , Institute of  
Organic Chemistry The National Hellenic Research Foundation  
Athens 116 35 Greece

The stoicheiometry of the reaction between  $\text{RMgX}$  and e.g. lithium naphthalene radical anion has been determined by the method of magnetic titration . When  $\text{X} = \text{Br}$  the stoicheiometry is 1:1 , and this result combined with product analysis and product characterization indicates that the reaction is as follows



Magnesium alkoxides as well as  $\text{RMgOR}$  resist reduction by radical anion rather strongly .

The stoicheiometry of interaction between radical anions bearing a functional group capable of acting as a strong ligand, such as **1** , with e.g.  $\text{TiX}_4$  ( $\text{X} = \text{Cl}, \text{OR}$  ) will be reported.



**1**

## STUDIES ON ORGANOMERCURY(II) COMPLEXES OF MALTOL

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G.S. Sodhi

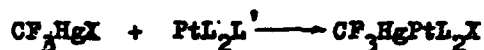
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A number of organomercury(II) complexes involving maltol of the type,  $\text{RHgL}$  [ $\text{R}$  = phenyl ( $\text{C}_6\text{H}_5$ ), *o*-, *p*-hydroxyphenyl (*o*-, *p*- $\text{HOC}_6\text{H}_4$ ), *p*-acetoxyphenyl (*p*- $\text{AcOC}_6\text{H}_4$ ), 2-furyl ( $2\text{-C}_4\text{H}_3\text{O}$ );  $\text{HL}$  = maltol] have been synthesised and characterised. Conductance measurements indicate that the complexes are non-electrolytes. From IR and UV studies, it is concluded that maltol acts as a bidentate ligand, coordinating to the mercury(II) ion through phenolic and carbonyl oxygen atoms.  $^1\text{H}$  and  $^{13}\text{C}$  NMR support the stoichiometry of the complexes. Fluorescence spectra has been recorded for *o*-, *p*- $\text{HOC}_6\text{H}_4\text{HgL}$  complexes. For  $\text{C}_6\text{H}_5\text{HgL}$ , *p*- $\text{HOC}_6\text{H}_4\text{HgL}$  and *p*- $\text{AcOC}_6\text{H}_4\text{HgL}$  complexes, thermal studies (TG and DSC) have been carried out and relevant kinetic and thermodynamic parameters have been enumerated. In addition, the fragmentation pattern of the complexes has been analysed on the basis of mass spectra.

REGIOSELECTIVITY OF THE  $L_2Pt(0)$  INSERTION INTO  
THE NONSYMMETRICAL ORGANOMERCURIALS

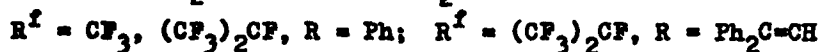
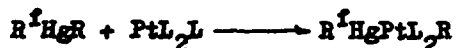
E.V. Masakaeva, V.V. Bashilov, V.I. Sokolov, Institute of Organo-  
Element Compounds, Academy of Sciences, Moscow, U.S.S.R.

Previously we have described the preparation of compounds such as cis-isomers  $(PPh_3)_2R^fM-HgR^f$ , wherein  $M=Pt, Pd$ . Now regioselectivity has been studied for the nonsymmetrical organomercurials  $R^fHgX$  and  $R^fHgR$  which differ by the electronic effects of both groups. With perfluoroalkylmercuric halides the insertion of  $L_2Pt$  occurred onto the Hg-Hal bond:



The presence of a Hg-Pt bond and the trans-arrangement of two phosphine ligands have been deduced from the  $^{31}P$  and  $^{19}F$  NMR spectra.

With the mercurials of type  $R^fHgR$  the insertion unexpectedly took place onto the Hg-R bond of the non-fluorinated group.



According to the  $^{31}P$  and  $^{19}F$  NMR spectra the insertion products for all non-symmetrical dialkylmercuries have cis-arrangement of both  $PPh_3$  ligands.

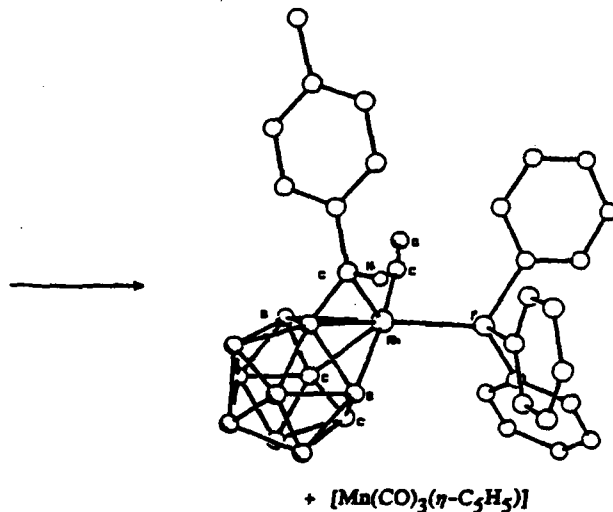
REACTIONS OF ANIONIC RHODACARBABORANES WITH  
ORGANOMETALLIC ELECTROPHILES

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and F. Gordon A. Stone

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Bristol BS8 1TS, Great Britain

The reactions of the anionic rhodacarbaborane complexes  $[(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})\text{RhL}_2]^-$  ( $\text{L}_2 = (\text{PPh}_3)(\text{CO}), (\text{CO})_2, (\eta^4\text{-cycloocta-1,5-diene})$ ) with a variety of organotransition metal electrophiles have been investigated. In particular, organometallic complexes have been chosen which feature exotic  $\pi$ -acid ligands, e.g., alkylidenes and alkylidyne.

The reactions which result will be discussed in terms of the non-innocence of the carbaborane and  $\pi$ -acid moieties. An illustration of this is provided by the following reaction:

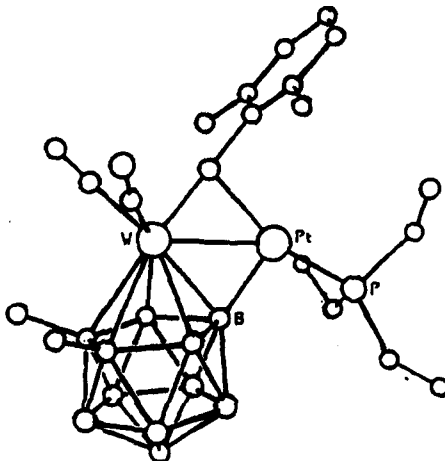


which involves the transfer and intramolecular hydroboration of a coordinated alkylidyne group.

HYDROGEN TRANSFER PROCESSES IN HETEROBIMETALLIC  
CARBABORANE COMPLEXESDavid D. Devore, Judith A.K. Howard, John C. Jeffery,  
Max U. Pilotti and F. Gordon A. StoneDepartment of Inorganic Chemistry, University of Bristol,  
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The salts  $[N(PPh_3)_2][W(\equiv CC_6H_4Me-4)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$  and  $[PtH(Me_2CO)(PEt_3)_2][BF_4]$  afford the dimetal compound  $[PtW(CO)_2(PEt_3)_2(\eta^6-C_2B_9H_8(CH_2C_6H_4Me-4)Me_2)]$  which features a novel hyper-closo metallacarborane configuration [1]. Fundamental to this unusual rearrangement is the intramolecular hydroboration of a  $\mu$ -alkylidyne ligand which ultimately becomes bound in a terminal manner to a boron vertex.

To better understand the processes involved, we have employed the sterically congested alkylidyne complex anion  $[W(\equiv CC_6H_3Me_2-2,6)(CO)_2(\eta^5-C_2B_9H_9Me_2)]^-$  1. It was anticipated that the bulky 2,6-dimethyl substituents might impede hydrogen transfer to the alkylidyne carbon and facilitate the interception of intermediates. Indeed, reaction of 1 with  $[PtH(Me_2CO)(PEt_3)_2]^+$  provides the bimetallic alkylidyne complex  $[PtW(\mu-CC_6H_3Me_2-2,6)(CO)_2(PEt_3)_2H(C_2B_9H_9Me_2)]$  2 which readily loses dihydrogen to provide the novel  $\sigma$ -carbaboranyl compound  $[PtW(\mu-CC_6H_3Me_2-2,6)(CO)_2(PEt_3)(\mu-\sigma-\eta^5-C_2B_9H_8Me_2)]$  3. The coordinatively unsaturated compound 3 forms adducts with CO,  $CN^tBu$  and hydrogen, the latter reaction being reversible, to, giving, respectively,  $[PtW(\mu-CC_6H_3Me_2-2,6)(CO)_2(PEt_3)(L)(\mu-\sigma-\eta^5-C_2B_9H_8Me_2)]$  (  $L = CO$  4,  $CN^tBu$  5 ), and 2.



3

[1] M.J. Attfield, J.A.K. Howard, A.N.de M. Jelfs, C.M. Nunn and F.G.A. Stone. *J. Chem. Soc., Dalton Trans.*, 1987, 2219.

SODIUM ALUMINUM HYDRIDE - PREPARATION AND APPLICATION

GUNNER E. NELSON  
ETHYL CORP., BATON ROUGE, LOUISIANA

WE REPORT THE DEVELOPMENT OF A FACILE SYNTHESIS OF SAH FROM THE ELEMENTS. PRELIMINARY RESULTS NEGATE THE INTERMEDIACY OF NAH IN THE PROCESS AS REPORTED EARLIER.

SAH IS USEFUL AS A REDUCING AGENT IN ITS OWN RIGHT AND CAN ALSO BE USED AS AN INTERMEDIATE IN THE PREPARATION OF REDUCING AGENTS IN COMMON USE SUCH AS  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ ,  $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2\text{H}_2$  AND  $\text{NaAlEt}_2\text{H}_2$ .

SAH REACTS READILY AND SELECTIVELY WITH  $\alpha$ -OLEFINS YIELDING THE DI-, TRI- AND TETRAALKYL ALUMINATES AS DESIRED. WE HAVE USED THE TETRAALKYL ALUMINATES AS ALKYLATING AGENTS IN THE PREPARATION OF ALKYL SILICON, -PHOSPHORUS AND -TIN COMPOUNDS.



REACTION OF ALKYLALUMINIUM COMPOUNDS WITH  
CARBON SUBOXIDE

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Umberto Vettori, Centro di Studio sulla Stabilit  e Reattivit  dei Composti  
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Trialkylaluminium compounds react with ketones giving products of addition,  
reduction and enolization reactions (1).

Reaction of trimethylaluminium with benzophenone was found to proceed through  
two distinct paths, depending upon the ratio of aluminiumalkyl to ketone (2).  
In continuation of our studies (3) on the reactivity of carbon suboxide, we  
have examined its reaction with trialkylaluminium compounds.

$C_3O_2$ , which presents two carbonylic groups, gives alkylated compounds.

In the reactions with trimethyl- and triethylaluminium in n-hexane, with ratios  
 $Al/C_3O_2 < 2$ , we have found the formation of a  $=C=O \cdots AlR_3$  adduct.  
With higher ratios ( $Al/C_3O_2 \geq 2$ ),  $(R_2Al)_2O$  was produced and, after hydro-  
lysis, two principal products,  $RCOCH_2COR$  and  $R_2C=CHCOR$ , were obtained  
( $R=Me, Et$ ).

Work supported by Ministero della Pubblica Istruzione (Roma).

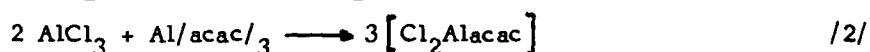
- (1) S. Pasynkiewicz, E. Sliwa - J. Organometal. Chem. 3, 121, (1965)
- (2) E.C. Ashby, J. Laemmle, H.M. Neumann - J. Am. Chem. Soc. 90, 5179, (1968)
- (3) L. Pandolfo, G. Paiaro, U. Vettori - Gazz. Chim. Ital. 11, 781, (1987);  
P. Ganis, G. Paiaro, L. Pandolfo, G. Valle, Organometallics 7, 210, (1988)

# SPECTROSCOPIC INVESTIGATION OF DICHLOROALUMINIUM ACETYLACETONATE

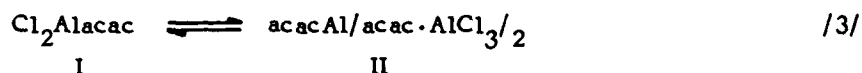
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00-661 Warszawa, Poland

We have found that dichloroaluminium acetylacetonate obtained by known methods <sup>1,2</sup> /illustrated by equations /1/ and /2/ / exist not only in the monomeric form  $\text{Cl}_2\text{Alacac}$ , like it was assumed previously <sup>1,2</sup>, but has a more complex structure



The structure of the dichloroaluminium acetylacetonate was studied by the means of variable temperature <sup>1</sup>H, <sup>13</sup>C and <sup>27</sup>Al NMR and IR spectroscopy. In the methylene chloride solution monomeric molecular complex  $\text{Cl}_2\text{Alacac}$  is in equilibrium with the trimer  $\text{acacAl/acac} \cdot \text{AlCl}_3/2$ .



Equilibrium /3/ depends on the temperature and the concentration of dichloroaluminium acetylacetonate. In diluted solution equilibrium is shifted to the left. Decrease of temperature and increase of concentration favours form II.

Our studies revealed that form II possesses three acetylacetonate ligands bonded to the central aluminium atom. One of them have a symmetrical chelate structure and two others - enol ether structure with complexed  $\text{AlCl}_3$  molecules.

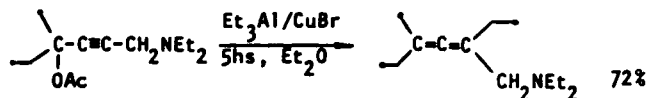
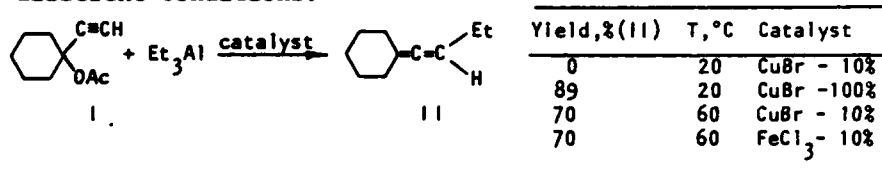
## References

1. W.R. Kroll, J. Kuntz, E. Brinbaum, J. Organomet. Chem., 26/1971/313.
2. K. Dowbor, Thesis, Warsaw Technical University, 1973.

# HIGHLY REACTIVE AND SELECTIVE ALUMOCOPPER REAGENTS APPLIED TO SYNTHESIS

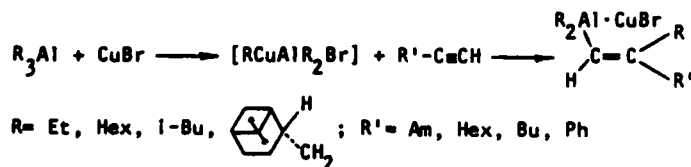
Kutchin A.V., Romanova T.Yu., Andreeva N.I., and Tolstikov G.A.  
Institute of Chemistry, Bashkirian Research Centre,  
Ural Department, USSR Acad.Sci., Ufa 450054 U.S.S.R.

To improve the reactivity and selectivity of organoaluminium reagents in substitution of propargyl substrates the alumocopper reagents prepared from trialkylalane and CuBr have been taken. Thus, the reaction of 1-diethylamino-4-acetoxy-4-methyl-2-hexyn with Et<sub>3</sub>Al·CuBr has been successful. This reaction fails under any different conditions.



The carbalumination of monosubstituted acetylenes with R<sub>3</sub>Al·CuBr proceeds at a good rate to reveal its satisfactory regioselectivity with the ration of α- and β-aluminated products as 9:1.

The alkenyl organometallic compounds thus obtained can be further usefully applied to synthesis of allyl alcohols, ethers, sulfides, etc. [1].



## Reference

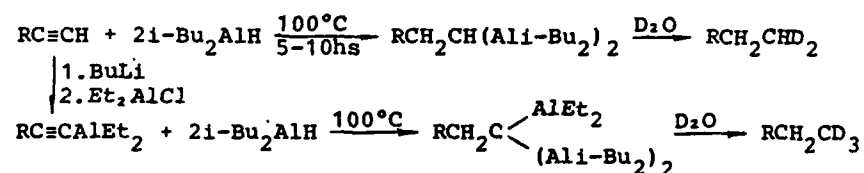
1. Kutchin A.V., Tolstikov G.A., and Andreeva N.I. Izv.AN SSSR Ser.Khim., 1987, 397.

THE DEVELOPMENT OF SYNTHETIC ROUTES TO AND SOME REACTIONS OF  
DI- AND TRIALUMINIUM OR ALUMOLITHIUM COMPOUNDS

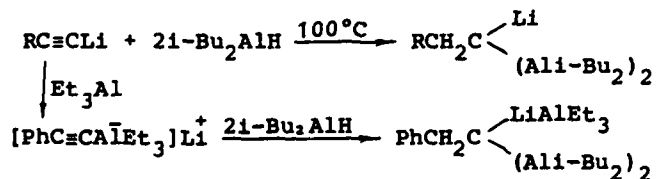
Kutchin A.V., Markova S.A., Gorobets E.V., and Tolstikov G.A.

Institute of Chemistry, Bashkirian Research Centre,  
Ural Department, USSR Acad.Sci., Ufa 450054 U.S.S.R.

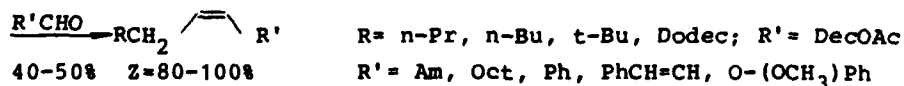
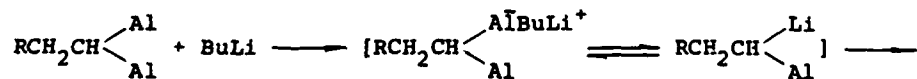
Polyorganometallics have been synthesized via double hydroalumination of terminal Al- and Li-acetylenes and acetylenides with diisobutyl-aluminium hydride. The reaction is over in 5-10hs at 100°C to reveal its high regioselectivity and complete conversion of substrates. The structures of the compounds obtained have been assigned by the deuterolysis and bromination products, the structures of which imply the geminal position of aluminium.



R = n-alkyl, t-Bu, c-hex, Ph



Gem-dialumoalkanes treated with n-BuLi are capable of attaching to the aldehyde carbonyl group to form olefins. Some pheromones can be thus synthesized due to high stereoselectivity of the above reaction (the content of Z reaches 100%).



ALUMINIUM-ORGANIC DERIVATIVES OF SOME FREE AND  
COORDINATED DIOXIMES

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Spiratos, "P. Poni" Institute of Macromolecular Chemistry,  
Aleea Grigore Ghica Vodă 41 A, R-6600, Iași, ROMANIA

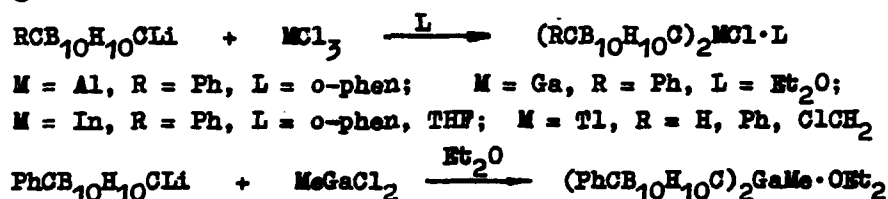
Aluminium- organic compounds of dimethyl- and diphenylglyoxime were obtained from the reaction of  $\text{Ni}(\text{DMGH})_2$ ,  $\text{Pd}(\text{DMGH})_2$ ,  $\text{Ni}(\text{DPGH})_2$  and  $\text{Pd}(\text{DPGH})_2$  (DMGH and DPGH being divalent radicals of dimethylglyoxime and diphenylglyoxime, respectively) with  $\text{R}_{3-n}\text{AlCl}_n$  derivatives ( $\text{R} = -\text{C}_2\text{H}_5$ ,  $1-\text{C}_4\text{H}_9$ ,  $-\text{C}_5\text{H}_6$ ,  $n = 1, 2$ ). The substitution of O-H...O bonds from the chelates by O-Al-O bridges determines the closing of some M-N-O-Al-O-N hexaatomic rings without carbon. The infrared absorption spectra evidenced the disappearing of the -OH absorption bands and the shift towards higher frequencies of the C=N and N-O absorption bands in dioximates, depending on the nature of the central metal ion, of the ligand and of the radical belonging to the aluminium atom. Also, the complexes have been studied using thermogravimetric method in order to obtain information concerning the thermal decomposition mechanism and the influence of the ligands on the thermal stability.

## CARBORANYL DERIVATIVES OF III GROUP NONTRANSITION METALS

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Carboranyl derivatives of III Group nontransition metals were obtained by interaction of carboranyllithium compounds with III Group metal halides or organometallic compounds with metal-halogen bond:



The interaction of Al, Ga, In and Tl trialkyls with carboranes in the presence of TMEDA, HMPA or DME leads either to metallation of carborane cage at a carbon atom or to degradation of a carborane cage.

Thus, the interaction of trimethylgallium with o- and 1-phenyl-o-carborane in benzene in the presence of TMEDA results in formation of undecaborate containing gallium. According to <sup>11</sup>B NMR data, in this anion Me<sub>2</sub>Ga fragment occupies the place of extra hydrogen over open face of carborane cluster.

The metallation of decachloro-o-carborane containing more acidic hydrogen of C-H bond than in unsubstituted carborane proceeds in the absence of TMEDA without degradation of carborane cage:



The interaction of o-carborane with (i-Bu)<sub>2</sub>AlH gives the mixture of carborane derivative with C-Al bond and products of carborane cage degradation.

## Disilanyl Metal Complexes: Preparation and Reactions

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The reaction of  $\text{Si}_2\text{Cl}_6$  with various sodium metallates 1a-c in cyclohexane leads to the formation of the pentachlorodisilanyl metal complexes 2a-c.

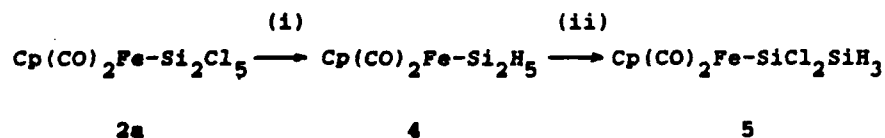


1a-c

	2   $\text{ML}_n$
a	$\text{Fe}(\text{CO})_2\text{Cp}$
b	$\text{Mo}(\text{CO})_3\text{Cp}$
c	$\text{W}(\text{CO})_3\text{Cp}$

2b,c show an unusual high tendency to decompose to the trichlorosilyl complexes  $\text{L}_n\text{M-SiCl}_3$  (3a-c) via silylene elimination both in the solid state and in solution. 2a shows this behaviour under photochemical conditions or in the presence of a Lewis base ( $\text{Me}_3\text{P}$ ,  $\text{Me}_3\text{N}$ ,  $\text{Et}_3\text{N}$ ).

Reaction of 2a with  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  yields the pentahydrido-disilanyl species 4, which in the presence of  $\text{CCl}_4$  undergoes regiospecific chlorination of the  $\alpha$ -silicon to generate the disilanyl species 5.

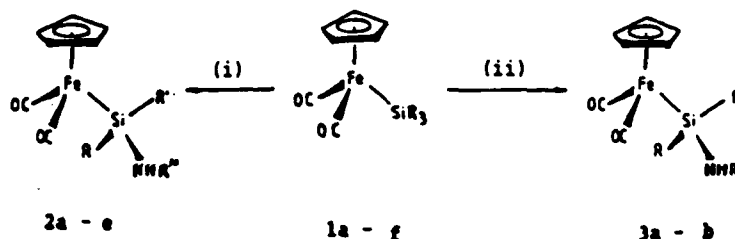


## Bifunctional Ferrio-aminosilanes

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The reaction of the ferrio-chlorosilanes  $\text{Cp}(\text{CO})_2\text{Fe-SiR}_x\text{Cl}_{3-x}$  ( $\text{R}=\text{H}, \text{Me}, \text{iPr}, \text{o-Tol}$ ) with primary amines  $\text{R}'\text{NH}_2$  and the corresponding amides  $\text{LiNHR}'$  ( $\text{R}'=\text{Me}, \text{tBu}, \text{Mes}$ ) results in formation of the ferrio-aminosilanes **2a-e**, **3a, b** having an iron bound bifunctional Si-N group. The thermal stability of **2a-e**, **3a, b** strongly depends on the nature of substituents both at the silicon and at the nitrogen.

i: excess  $\text{R}'\text{NH}_2$ , ii:  $\text{R}'\text{NHLi}$ 

1:  $\text{SiR}_3 = \text{SiHCl}_2$  (a),  $\text{SiMeCl}_2$  (b),  $\text{SiMe(H)Cl}$  (c),  $\text{Si(iPr)HCl}$  (d),  $\text{Si(iPr)Cl}_2$  (e),  $\text{Si(o-Tol)HCl}$  (f).

2:  $\text{SiRR}'(\text{NHR}') = \text{SiH}(\text{NHtBu})_2$  (a),  $\text{SiMeCl}(\text{NHtBu})$  (b),  $\text{SiMe(H)NHtBu}$  (c),  $\text{Si(iPr)H}(\text{NHMe})$  (d),  $\text{Si(iPr)}(\text{NHMe})_2$  (e).

3:  $\text{SiR}_2(\text{NHR}') = \text{SiMe(H)NHMe}$  (a),  $\text{Si(o-Tol)H}(\text{NHMe})$  (b).

$\text{CO/R}_3\text{P}$ -exchange reactions at the iron centre are presented, as well as ligand exchange experiments at the silicon, leading to useful precursors for the generation of silaimine complexes  $\text{Cp(L)}_2\text{Fe-Si(R)=NR}'$ .



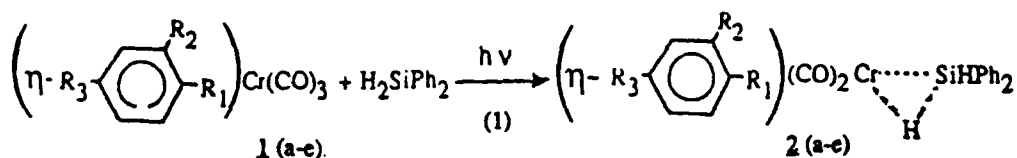
Transition metal Hydrosilyl complexes,  $(\eta\text{-arene})(\text{CO})_2\text{Cr}(\text{H})\text{SiHPh}_2$   
2e/3c bond, Cr-H-Si. From Si-H to Si-O-Si.

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Ecole Nationale Supérieure de Chimie de Paris - U.A. 403

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Diphenylsilane reacts photochemically on  $(\eta\text{-arene})\text{tricarbonylchromium complexes}$ , **1** (a-e), to hydrosilyl derivatives, **2** (a-e), characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  nmr.



$$^2J(\text{Si-Cr-H})/\text{Hz}$$

<b>1a,2a</b> $R_1 = R_2 = \text{CH}_3$ ; $H = R_3$	$80 \pm 0,5$
<b>1b,2b</b> $R_1 = \text{CH}_2\text{N}(\text{CH}_3)_2$ ; $R_2 = R_3 = \text{H}$	$79 \pm 2$
<b>1c,2c</b> $R_1 = R_2 = R_3 = \text{H}$	$80 \pm 1$
<b>1d,2d</b> $R_1 = \text{COOCH}_3$ ; $R_2 = R_3 = \text{H}$	$81 \pm 1$
<b>1e,2e</b> $R_1 = R_3 = \text{COOCH}_3$ ; $R_2 = \text{H}$	$82,5 \pm 2$

The high value of  $^2J(\text{Si-Cr-H})$ ,  $\approx 80\text{Hz}$ , confirms the presence of 2 electron/3 center bond  $-(\text{Cr-Si-H})$ .  $^2J(\text{Si-Cr-H})$ ,  $^1J(\text{Si-H})$  and  $^{29}\text{Si}$  are examined depending on Hammett's  $\sigma_{\text{para}}$ .

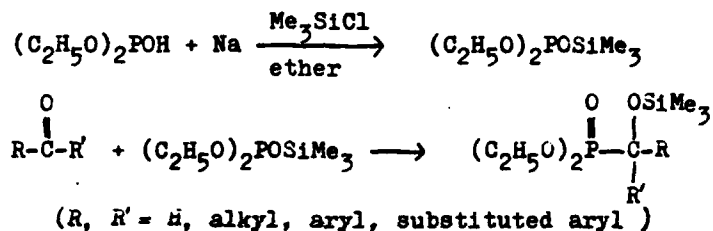
The hydrosilation (1) is accompanied by 1,1,3,3 tetraphenyldisiloxane formation. In the presence of **2** (a-e), it oligomerizes to polysiloxanes:  $\text{HSiPh}_2(\text{OSiPh}_2)_n\text{H}$ ,  $n = 2-6$  and  $(\text{Ph}_2\text{SiO})_n$ ,  $n = 3,4$ .

Studies On Synthesis Of Dialkyl  
 $\alpha$ -Trimethylsilyloxyalkylphosphonates

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Using Dialkyl  $\alpha$ -Trimethylsilyloxyalkylphosphonates as synthetic intermediates can prepare many acetones and  $\alpha$ -hydroxyacetones both are with complex structures.

The report of research works concerning synthesis of contained phosphorus-silicon compounds is real small. The new method which we present adopt phosphorus-silicon reagents proceeding addition reaction with carbonyl compounds to prepare Dialkyl  $\alpha$ -Trimethylsilyloxyalkylphosphonates, gaining 12 compounds successfully which have not reported yet from references. This method is better than the original, as it possesses simple operation of reaction, higher yield and other merit. All products have been conformed by IR and NMR spectrums. It contain two reactions:



This paper reports reaction conditions, and make a preliminary discussion about the factors of affecting reaction.

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PREPARATION AND IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR SPECTRAL STUDIES OF  
TRIORGANOTIN(IV) DERIVATIVES OF N-FORMYL-L-PHENYLALANINE AND  
N-FORMYL-L-PHENYLALANYLGLYCINE.

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ABSTRACT

Preparation and structure elucidation studies of some diorganotin and triorganotin complexes of amino acids and dipeptides have already been reported (1-9). Complexes  $\text{R}_3\text{SnX}$  ( $\text{R}=\text{Me}$ ,  $n\text{-Pr}$ ,  $n\text{-Bu}$ , cyclohexyl, phenyl,  $\text{X}$  = anion of  $N$ -formyl-L-phenylalanine and  $N$ -formyl-L-phenylalanylglycine) have been prepared by reacting triorganotin(IV) chlorides with sodium salts of the  $N$ -formyl-L-phenylalanine and  $N$ -formyl-L-phenylalanylglycine or with the acids in the presence of triethylamine. All the complexes are weak polymers in the solid state with a unidentate carboxylate and a weak intermolecular donor-acceptor  $\text{NHCC}\dots\text{Sn}(\text{R}_3)\text{O}$  bond. In non-coordinating solvents ( $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6$ ) all the complexes are monomeric and tetrahedral, in coordinating solvents (DMSO) coordination by one molecule of solvent occurs to form trans trigonal bipyramidal complexes as revealed by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR studies.

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# ORGANOTIN(IV) DERIVATIVES OF BIS(PYRAZOL-1-YL)ALKANES

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The series of organotin(IV) derivatives  $R_aSnX_b$  ( $X$  = halogen;  $R$  = Me, Ph :  $a+b = 4$ ) was used in order to investigate the donor properties of several bis(pyrazolyl) alkanes,  $(pz)_2CR_2$ :  $L_1$  ( $R$  = H,  $pzH$  = pyrazole),  $L_2$  ( $R$  = H,  $pzH$  = 3,5- dimethylpyrazole),  $L_3$  ( $R$  = H,  $pzH$  = 4-nitropyrazole),  $L_4$  ( $R$  = Me,  $pzH$  = pyrazole), and  $L_5$  ( $R$  = H,  $pzH$  = 3,5-di-~~tert~~-butylpyrazole).

If  $a \leq 2$  in most cases, but  $L_3$  and  $L_5$ , an 1:1 adduct was isolated and characterized. The behaviour in solution was studied by  $^1H$ ,  $^{13}C$ , or  $^{119}Sn$  nmr, by conductivity and by molecular weight determinations by osmometry.

While in solution (acetone or dimethylsulphoxide), the adducts of  $L_1$  are non-electrolyte and dissociate into the starting components (1), complex equilibria are found in the isolated derivatives of the more basic ( $L_2$ ) or more sterically demanding ligands (e.g.  $L_4$ ).

The combined evidence suggest that in several cases e.g. when  $a = 3$  and  $X = Cl$ , several species co-exist in the solution owing to solvation, ionization, and/or positional isomerism.

Work supported by CNR and Ministero P.I..

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## SYNTHESIS OF ARYL COMPLEXES OF Rh(III), Tl(III) AND Sn(IV).

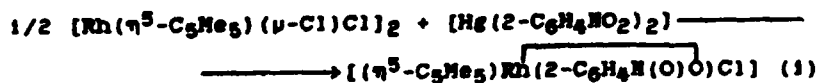
-Jose Vicente, Jose-Antonio Abad, Maria-Teresa Chicote,  
Juan-Francisco Gutierrez-Jugo, Carmen Ramirez de Arellano.  
Departamento de Quimica Inorganica, Universidad de Murcia,  
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-Peter G. Jones, Institut für Anorganische Chemie der  
Universität, Tammannstrasse 4, 3400 Göttingen, W. Germany.

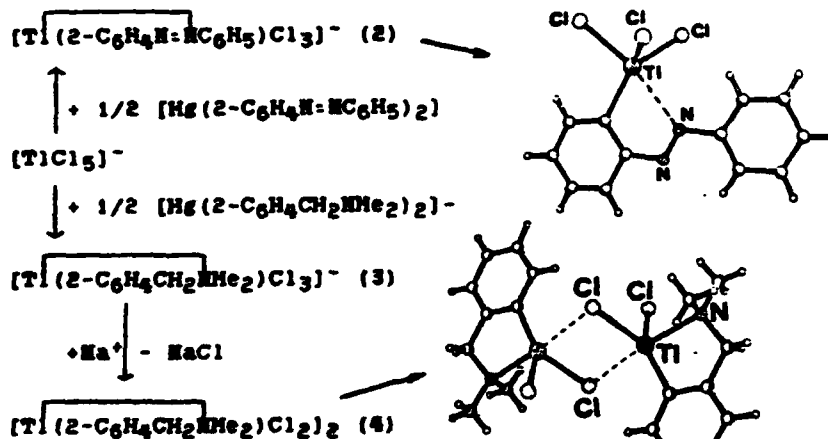
-Giancarlo Pelizzi, Istituto di Chimica Generale ed  
Inorganica, Università di Parma. 43100 Parma. Italy.

The following transmetalation reactions allow to  
prepare aryl complexes of:

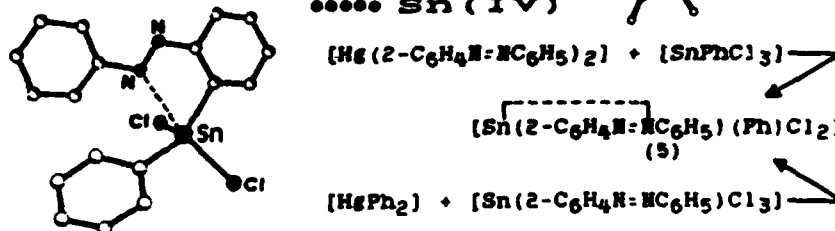
## \*\*\*\*\* Rh (III)



## \*\*\*\*\* Tl (III)



## \*\*\*\*\* Sn (IV)



Reactions with neutral and anionic ligands of complexes  
(1)-(5) are described.

ELUCIDATION OF THE GEOMETRY AND CONFIGURATION OF  
ORGANOTIN (IV) COMPLEXES OF SCHIFF BASES OF AMINO ACIDS

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The present paper is a report on the synthesis, characterization and geometrical features of penta-coordinated dibutyl tin (IV) complexes of Schiff bases derived by the condensation of Amino acids viz, Glycine  $\beta$ -alanine and Anthranilic acid with 2-Hydroxy-1-naphthaldehyde and Benzoin. The conductance measurements in DMF show these complexes to be non-electrolytes and the molecular weight determinations indicate their monomeric nature.

On the basis of UV, IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  &  $^{119}\text{Sn}$ ), Mössbauer spectra along with the mass spectral fragmentation pattern trigonal bipyramidal geometry is proposed. The nitrogen atom probably occupies the axial site, while the remaining two oxygen atoms and the dibutyl groups rest in an equatorial plane.

Synthesis and characterization of organotin(IV) complexes of  
thiohydrazides and thiohydrazone

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Complexes of 2-furanthiocarboxyhydrazide (Hfth), 4-hydroxyphenyl-thiocarboxyhydrazide (Hoth) and salicylaldehyde-2-furanthiocarboxyhydrazone ( $H_2L$ ) have been prepared by the reactions of  $Bu_2SnO$  and  $Ph_2SnCl_2$  taken in appropriate molar ratio and refluxing the reaction mixture for several hours in non-aqueous media; sodium was used in the preparation of deprotonated complexes. The resulting complexes have been characterized on the basis of elemental analysis, molar conductance, melting point and various physico-chemical techniques. The complexes have been found to melt between 64 to 210 C, the corresponding dibutyl tin(IV) complexes have lower melting points than the diphenyl tin(IV) complexes. IR coupled with  $^1H$  and  $^{13}C$  NMR spectra suggest bonding through thione/thiol sulphur and amino nitrogen.  $^{119}Sn$  spectra of some compounds have also been studied in order to get the structural information.

## SYNTHESIS OF ORGANOTIN DERIVATIVES OF BIOLOGICAL INTEREST

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Several organotin derivatives of biological interest have been synthesized starting from diorganotin dihalides (e.g. dimethyl-, dibutyl- and diphenyltin dichloride) or diorganotin-oxides (e.g. dibutyltin oxide) and carboxylic acids and hydroxycarboxylic acids or their salts. The structure of these compounds has been examined by IR, NMR and mass spectrometry. The possibilities of using the prepared compounds as antitumor agents are discussed in comparison with known organotin antitumor agents /1-4/.

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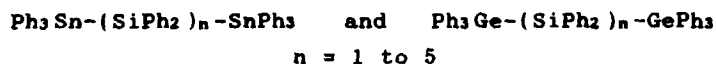


**DEPENDENCE BETWEEN STRUCTURE AND ELECTRONIC TRANSITIONS  
IN GePh<sub>3</sub>- AND SnPh<sub>3</sub>-TERMINATED POLYSILANES**

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In the last decade the photochemical behaviour of organosilicon polymers gained industrial interest [1]. The  $\sigma$ -bonded Si<sub>n</sub> chains are thermally very stable and show strong UV absorption in the range 300-350 nm. Related Sn<sub>n</sub> chains show even stronger electronic absorption extending to the visible range [2], their thermal stability is much lower however. To combine both properties, electronic absorption at longer wavelength and thermal stability, we synthesized some model oligomers. These compounds form two series of linear Polysilanes



produced in good yields by coupling of the corresponding dichloro polysilanes with stannyl- and germyllithium reagents in thf at -75 °C.

As found by X-ray structure determinations, all chain conformations are antiperiplanar. The values of the electronic absorption maxima and the NMR chemical shifts and couplings for <sup>29</sup>Si and <sup>119</sup>Sn are strong dependent on chain length and slightly dependent upon bond lengths and angles (distance ranges Si-Si 235-241, Ge-Si 242-243 and Sn-Si 259-260 pm).

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PREPARATION AND SPECTROSCOPIC STUDIES  
OF DI-ISO-PROPYLTIN DICHLORIDE AND  
ITS ADDUCTS WITH SOME N-DONORS.

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and

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Di-iso-propyltin dichloride has been prepared by the redistribution reaction method in good yield and characterised by elemental analysis, molecular weight determination,  $^1\text{H}$  NMR, IR and mass spectroscopically. X-ray data of the above compound is well in agreement with the tetragonal symmetry to give the lattice constants  $a = 12.9751 \text{ \AA}$ ,  $c = 15.7359 \text{ \AA}$  and cell volume  $V = 2649.1894 \text{ \AA}^3$ . It has been found to form 1:2 (acid/base) adducts with unidentate ligands viz triethylamine, quinoline,  $\beta$ -naphthylamine and O-tolidine and 1:1 adduct with 2,2'-bipyridyl. Their molar conductance values show that they are weak electrolytes in nitrobenzene while their molecular weight determinations indicate that they exist as monomers with small dissociation. Their IR in the range  $4000\text{--}200\text{cm}^{-1}$  and  $^1\text{H}$  NMR have also been studied.

## STRUCTURAL FEATURES OF TIN(IV) PYRROLYLTHIOCARBAMATES

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With a view to understand the factors influencing the coordination number, the geometry of the coordination, the coordination polyhedron and the isomer formed, crystal and molecular structures of the complete series of tin(IV) pyrrolylthiocarbamates,  $\text{Ph}_3\text{SnL}$ ,  $\text{Me}_2\text{SnL}_2$ ,  $\text{PhSnL}_3$  and  $\text{SnL}_4$  (with tin:ligand ratio 1 to 4) have been examined. While the coordination environment around tin varies from  $\text{Ph}_3\text{SnL}$  to  $\text{SnL}_4$  complex, the nature of the coordination of monothiocarbamate ligand smoothly changes from simple sulfur-bonded to typical bidentate mode. The Sn-S bond distances are comparably similar. However, it is Sn-O interaction which becomes prominent with the gradual incorporation of the ligand around the tin centre. The presence of aromatic pyrrole system destabilizes the double bonded canonical form (  $\text{N}^+=\text{C} \begin{smallmatrix} \text{O}^- \\ \diagup \end{smallmatrix} \begin{smallmatrix} \text{S}^- \\ \diagdown \end{smallmatrix}$  ) of the ligand. It is the mercaptide form which predominantly contributes to the ground state electronic structure of pyrrolylthiocarbamate in these complexes. Spectroscopic evidence particularly multinuclear NMR data suggests little structural changes in the solution.

PHOSPHINOMETHANIDE LIGANDS IN MAIN GROUP ELEMENT COMPLEXES:  
UNUSUAL BONDING, COORDINATION NUMBERS AND OXIDATION STATES

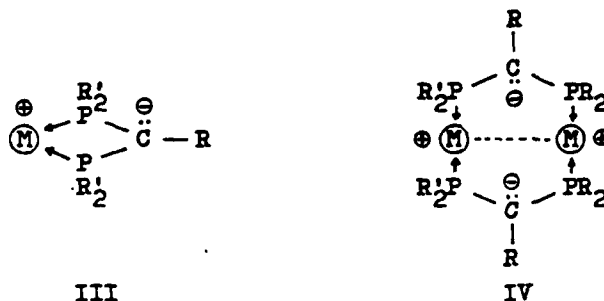
243

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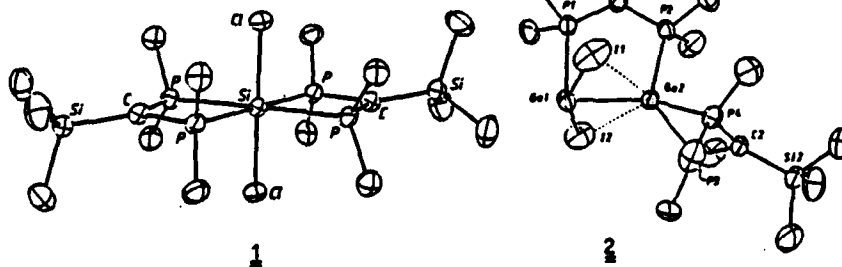
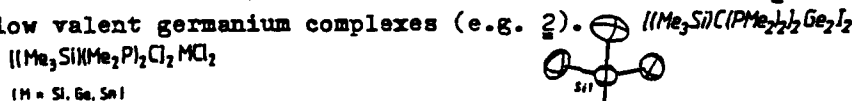
Monophosphinomethanides I and Diphosphinomethanides II



are ambidentate ligands exhibiting unusual properties and unusual bonding modes. Particularly interesting are diphosphinomethanides II,



which on coordination to main group element acceptors stabilize high phosphine coordination numbers and/or low oxidation states due to the betaine-type character of these complexes. Examples are given, inter alia, for hexacoordinated silicon (e.g. 1) and for low valent germanium complexes (e.g. 2).



REACTION OF TRIBUTYLTIN HYDRIDE  
WITH CHLORINATED ESTERS

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The reaction of tributyltin hydride with esters have been shown to yield mainly corresponding hydrocarbons and stannyl esters.<sup>1</sup> This reaction requires quite drastic conditions, so it is possible to reduce some functional groups in an ester before the ester function. Thus, it is possible to reduce cleanly halogens (except F) in the ester provided that there are not  $\alpha$  halogens in both acyl and alkyl group of the ester.  $\alpha$  Halogens give rise to the break of the carbon-oxygen bond and subsequent reactions.

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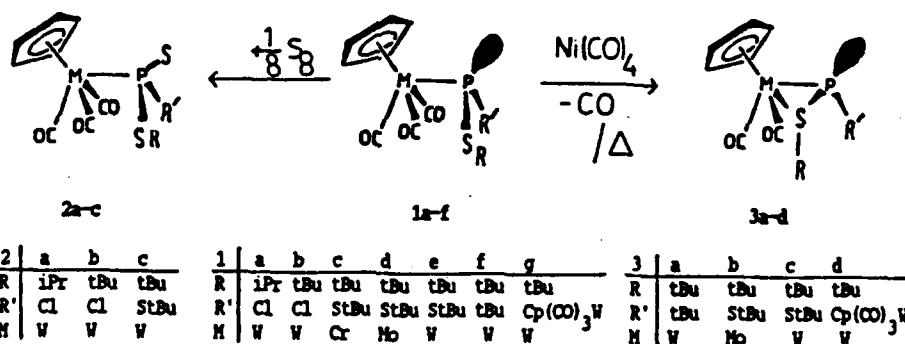
Complexes with a Thioalkyl-Bridged M-P-Bond from Metallo-  
(alkylthio)phosphanes

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Metallation of alkylthio(chloro)phosphanes  $\text{ClP(R')S-R}$  ( $\text{R} = \text{iPr}, \text{tBu}$ ;  $\text{R}' = \text{tBu}, \text{StBu}$ ) with  $\text{Na[M(CO)}_3\text{Cp]}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) yields the metallo-(alkylthio)chloro-, metallo-bis(alkylthio)-, metallo-(alkylthio)-alkyl-posphanes (1a-f) or the bismetallo-(alkylthio)phosphane (3g) respectively. Metallo-(alkylthio)thiophosphoranes (2a-c) are obtained from 1a-c via oxidation with elementary sulfur.



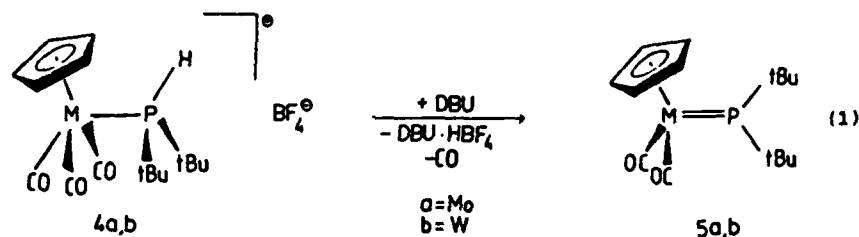
Due to the bulkiness of the P-bonded non metal ligands the metallo-(alkylthio)phosphanes 1d-g can be easily decarbonylated to the corresponding metallacyclopropanes (3a-d) either thermally or via reaction with  $\text{Ni(CO)}_4$ . 3a-d can be described as S-donor stabilized metal to phosphorus double bonded species. The combination of a thioalkyl ligand with a bulky amino group causes preference of the M=P-Isomer. This fact is demonstrated by the existence of  $\text{Cp(CO)}_2\text{W}=\text{P(TMPip)S-iPr}$  obtained from  $\text{Cp(CO)}_2\text{W}=\text{P(TMPip)Cl}$  and  $\text{NaS-iPr}$ .

THE METAL PHOSPHORUS DOUBLE BONDED COMPLEX  $\text{Cp}(\text{CO})_2\text{M}=\text{P}^t\text{Bu}_2$ :  
NOVEL SYNTHESIS AND REACTIONS WITH TRANSITION METAL HALIDES.

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The successive reaction of the metalhydrides  $\text{Cp}(\text{CO})_3\text{M}-\text{H}$  (1a,b) with  $[\text{Ph}_3\text{C}]\text{BF}_4$  (2) and  $^t\text{Bu}_2\text{PH}$  (3) leads to the cationic complexes 4a,b, which can be deprotonated by DBU to give the metal phosphorus double bonded species 5a,b.<sup>1)</sup>



(1) represents a novel, in comparison to the dehydrohalogenation and decarbonylation route<sup>2)</sup> more versatile procedure for the generation of phosphorus metal double bonded complexes.

The reactivity of the  $\text{M}=\text{P}$ -complexes will be demonstrated by the addition of  $\text{Te}$ ,  $\text{CuCl}$ ,  $\text{AgCl}$ ,  $\text{AuCl}(\text{PPh}_3)$  and  $\text{HgCl}_2$  to the  $\text{W}=\text{P}$  bond of 5b. The structures of the  $\text{Te}$ - or the  $\text{AuCl}(\text{PPh}_3)$ -adduct respectively will be presented.

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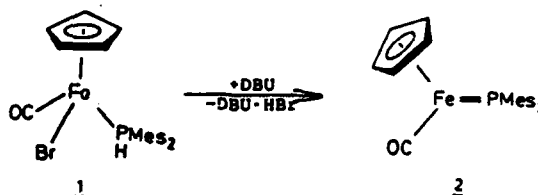
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SYNTHESIS AND REACTIVITY OF THE IRON-PHOSPHORUS DOUBLE BONDED SPECIES  $\text{Cp}(\text{CO})\text{Fe}=\text{PMe}_2$

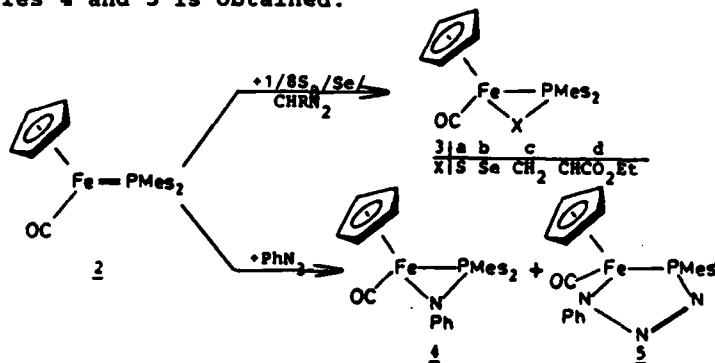
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Treatment of 1, obtained via irradiation of  $\text{Cp}(\text{CO})_2\text{FeBr}$  with  $\text{Me}_2\text{PH}$ , with DBU yields the phosphorous iron double bonded species 2.



2 shows high activity towards nucleophiles and electrophiles. Reaction with sulfur, selenium or diazoalkanes leads to the formation of the metallocyclopropanes 3a-d. With phenylazide a mixture of the three and five membered ring species 4 and 5 is obtained.



The reaction of 2 with isonitriles,  $\text{CS}_2$ , dienes and acetylenes will be reported.



ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY OF ACYCLIC DITERTIARY  
PHOSHPINES AND ARSINES

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The He(I) photoelectron spectra of  $\text{Ph}_2\text{X}-(\text{CH}_2)_n-\text{YPh}_2$  compounds  
(X, Y = P or As,  $n = 1$  or  $2$ ) - frequently used as complexing  
ligands in transition metal chemistry - have been recorded and  
interpreted. The gaseous phase molecular geometries are not  
available the only experimental data are provided by the NMR  
studies of  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (1).

The low energy part of the spectra are very similar to each others.  
The maximum of the first weak band in the region of 7.75 and 8.15 eV  
refers to the ionization of heteroatom lone pair. The second, more  
intense, band system showing maximum at about 9 eV can be assigned  
to the ionization of the benzene  $\pi$ -system. The third less intense  
band at about 10.35-10.85 eV originates from the ionization of  
X(and/or Y)-C  $\sigma$ -skeleton. The interpretation of the spectra is in  
good agreement with the ultraviolet photoelectron spectroscopy  
studies of their tungsten complexes (2) and that of related  
molecules (3).

According to our results there is no sizeable interaction between  
heteroatom lone pairs, furthermore  $\pi/\pi$  and  $n/\pi$  interactions are  
similar to those measured in  $\text{Ph}_3\text{X}$  (or Y).

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## Ferrio-dimethylphosphanes

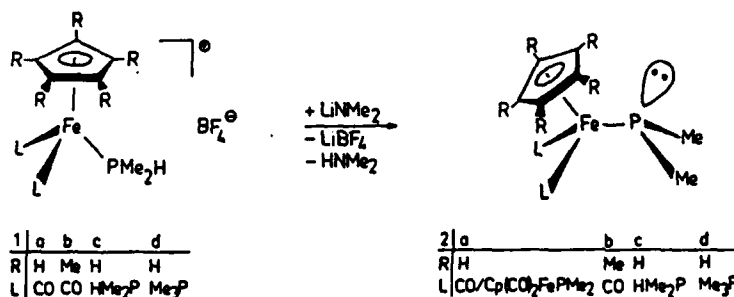
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Stable metallo-dimethylphosphanes are available via the deprotonation of the PH-functional cationic iron salts  $[(C_5R_5)(L)_2(HMe_2P)Fe]BF_4$  ( $R = H, Me$ ;  $L = CO, HMe_2P, Me_3P$ ) (1a-d).

While  $[Cp(CO)_2(HMe_2P)Fe]BF_4$  (1a) yields the dinuclear ferrio-phosphan 2a, the analogous reaction of 1b-d leads to the monomeric phosphido complexes 2b-d, as a consequence of the stabilizing effect of the electron releasing  $C_5Me_5$  unit or the phosphane ligands respectively. The mechanism for the formation of 2a involves the intermediate formation of the metallo-phosphane "Cp(CO)<sub>2</sub>Fe-PMe<sub>2</sub>".



2a-d show pronounced reactivity at the phosphido phosphorus towards diverse electrophilic reagents (HCl, MeI, AgCl etc.), a behaviour, which is characteristic for metallo-phosphanes 1a-c).

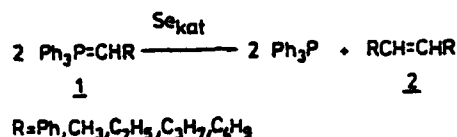
The reactions of 2a,b with some transition metal complexes  $[Cp(CO)_3MX]$  ( $M = Mo, W$ ;  $X = H, Cl, Me$ );  $[Cp(CO)_3Fe]BF_4$ ;  $Pt(PPh_3)_2(C_2H_4)$  etc. ] will be reported.

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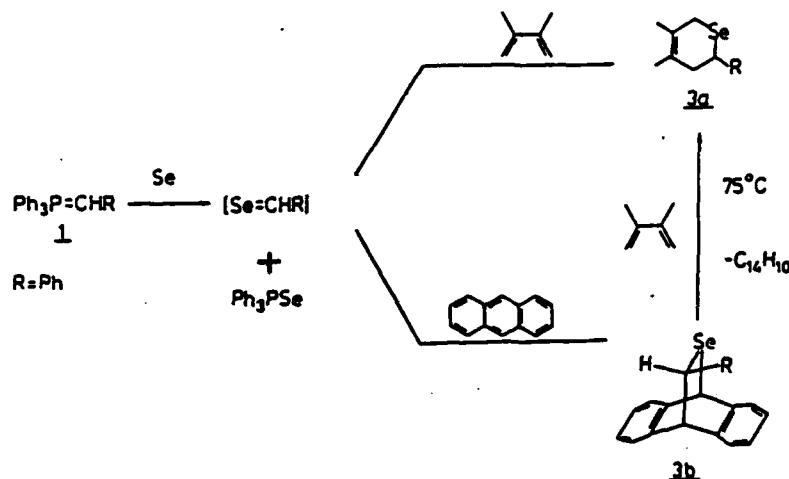
**Selenoketones and -aldehydes by Reaction of Phosphorus Ylides with Elemental Selenium**

**Regina Hock, Gerhard Erker**  
 Institut für Organische Chemie der Universität Würzburg  
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The reaction of alkylidenetriphenylphosphoranes **1** with catalytic amounts of elemental selenium yields the olefins **2** and triphenylphosphine. A mechanism similar to the Wittig olefination reaction is proposed, involving selenoaldehyde intermediate.



From the reaction of  $\text{Ph}_3\text{P}=\text{CHPh}$  **1a** with two equivalents of selenium in the presence of conjugated dienes, the Diels-Alder products **3** of the seleno-aldehyde intermediate were obtained <sup>1)</sup>.



From the stoichiometric reaction of  $\text{Ph}_3\text{P}=\text{Ph}_2$  **1f** with Se selenobenzophenone was isolated as a brightly green coloured solid. At ambient temperature it forms the Diels-Alder adducts with various conjugated olefins.

1) G. Erker, R. Hock, R. Nolte. J. Am. Chem. Soc. 110 (1988), 624

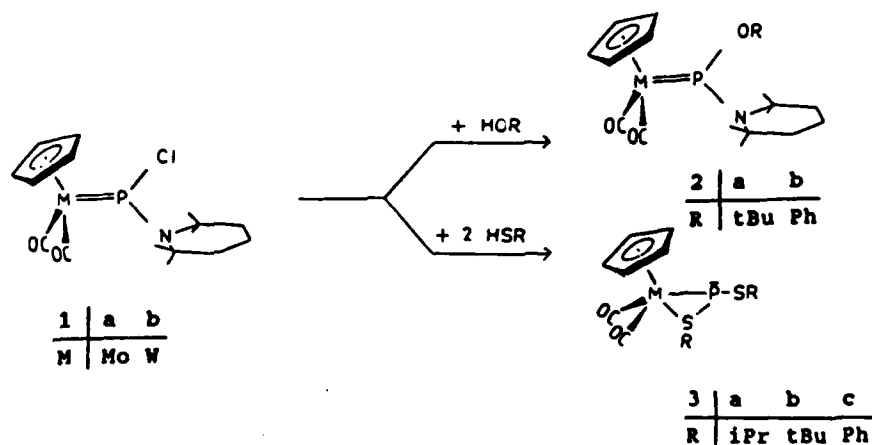
**FUNCTIONAL METAL PHOSPHORUS DOUBLE BOND COMPLEXES**  
 **$\text{Cp}(\text{CO})_2\text{M}=\text{P}(\text{NR}_2)$  (M = Mo, W): EXCHANGE REACTIONS AT THE**  
**PHOSPHORUS**

U.-A. Hirth und W. Malisch, Institut für Anorganische Chemie  
 der Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG

Metallation of the aminodichlorophosphane  $\text{R}_2\text{NPCl}_2$  ( $\text{R}_2\text{N}$  = 2.2.6.6.-tetramethylpiperidine) with  $\text{Na}[\text{M}(\text{CO})_3\text{Cp}]$  (M = Mo, W) yields the metallo-aminochlorophosphanes  $\text{Cp}(\text{CO})_2\text{M}=\text{P}(\text{NR}_2)\text{Cl}$ , which can be easily converted to the corresponding metal phosphorus double bond complexes 1a,b via decarbonylation.

The reactions of 1b with tert.-butanole and diverse phenols in presence of  $\text{Et}_3\text{N}$  leads to the formation of the alkoxy-derivates 2a,b.

With mercaptanes substitution of both the chlorine and the aminoligand is observed to give the threemembered heterocycles 3a-c, in which an organylthio ligand is bridging the metal phosphorus bond.



Futher experiments to exchange the P-bonded chlorine atom against diverse nucleophiles will be presented.

## ORGANOANTIMONY COMPOUNDS AS FLAME RETARDANTS FOR POLYPROPYLENE.

A.C. Mishra<sup>a</sup>, P. Bajaj<sup>b</sup> and N.K. Jha<sup>a</sup><sup>a</sup> Department of Chemistry, I.I.T., New Delhi-110016, INDIA<sup>b</sup> Department of Textile Technology.

Antimony oxide in conjunction with organohalogen compounds is known to have good flame retardant property for many organic polymers including polypropylene. Triphenyl stibine can also serve in place of antimony trioxide. As an alternative of a mixture of antimony compound and an organic halogen compound we have synthesized and characterised a new series of antimony halogen based flame retardants in the form of halogen derivatives of organoantimony (V) compounds e.g. triphenylstibine dibromide and triphenyl antimony (V) derivatives of tribromo-, trichloro- and pentachlorophenols. The performance of these compounds as flame retardants for polypropylene has been evaluated by measuring limiting oxygen index, vertical flame test and smoke density of the flame retardant-polypropylene systems. The LOI of polypropylene was raised from 18 to approximately 30 in the flame retardant loaded polypropylene systems. Triphenyl stibine dibromide proved to be the most effective flame retardant among all the organoantimony (V) compounds tested. The effect of loading on the processability and mechanical properties of the flame retardant loaded propylene systems has also been evaluated and is reported.

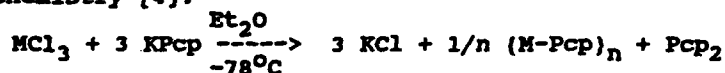
**Formation of Decamethyl-bis-Cyclopentadiene by Reductive  
Elimination: A General Feature in Main Group Element Chemistry?**

J.Lorberth, Th.F.Berlitz, S.H. Shin, U.Müller and H.Sinning,

Fachbereich Chemie, Philipps-University, Hans-Meerwein-Strasse,  
D-3550 Marburg/Lahn, West Germany.

Tris-cyclopentadienyls of the heavier elements in group 13, viz. InCp<sub>3</sub>, have an unusual structure [1] or are not known at all for Tl, where only Tl(I) compounds exist [2]. Tetracoordinate cyclopentadienyls of group 14 have regular tetrahedral structures and tris-cyclopentadienyls of group 15 are trigonal pyramidal shaped molecules in the case of Antimony [3] and believed to be isomorphous for Arsenic and Bismuth.

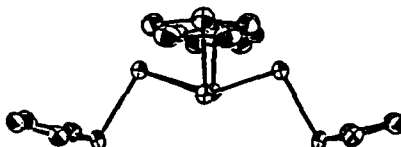
Reaction of Antimony and Bismuth trihalides with the potassium salt of pentamethylcyclopentadiene (abbrev.: Pcp) yielded metal-metal-bonded main group element clusters with the elimination of decamethyl-bis-cyclopentadiene, a molecule first observed in organotin chemistry [4]:



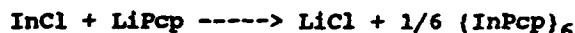
M = Sb, Bi: n = 4

M = In : n = 6

M = Tl : n = ?



The hexameric Indium compound [InPcp]<sub>6</sub> was already described in the literature [5] by the reaction



We report on the structures of (SbPcp)<sub>4</sub>, (BiPcp)<sub>4</sub>, Tl(Pcp)<sub>3</sub> and the elusive decamethyl-bis-cyclopentadiene, C<sub>20</sub>H<sub>30</sub>, obtained by reductive elimination from MPcp<sub>3</sub> and consecutive C-C-bond formation; a radical reaction pathway is substantiated by EPR spectroscopy.

Reactions of (SbPcp)<sub>4</sub> and (BiPcp)<sub>4</sub> with BF<sub>3</sub> and other reagents are reported.

- [1] F.W.B.Einstein, M.M.Gilbert and D.G.Tuck, Inorg.Chem., 11 (1972) 2832.
- [2] H.Schumann, C.Janiak, J.Pickardt and U.Börner, Angew.Chem., 99 (1987) 788.
- [3] M.Birkhahn, P.Krommes, W.Massa and J.Lorberth, J.Organomet. Chem., 208 (1981) 161.
- [4] P.Jutzi and F.Kohl, J.Organomet.Chem., 164 (1979) 141.
- [5] O.T.Beachley, Jr., M.R.Churchill, J.C.Fettingner, J.C.Pazik and L.Victoriano, J.Amer.Chem.Soc., 108 (1986) 4666.

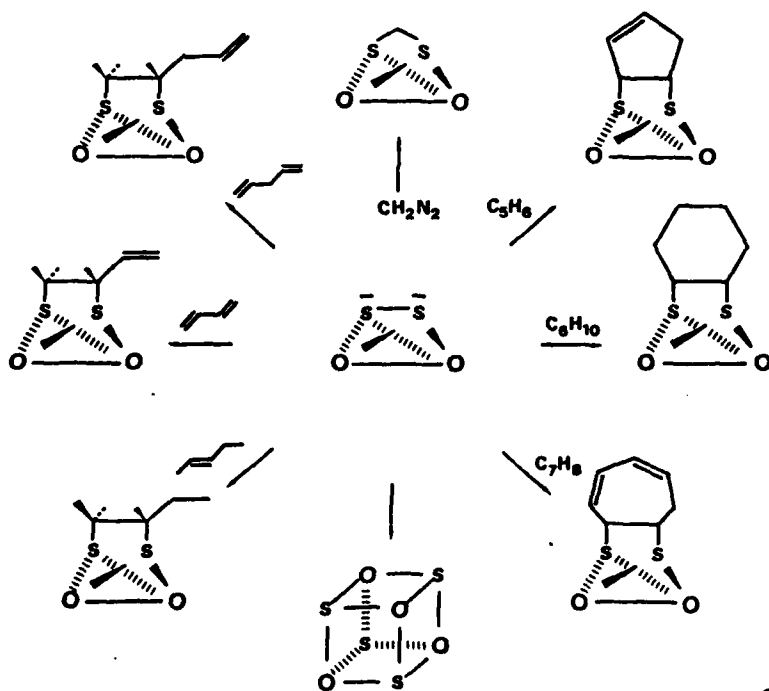
PHOTOINDUCED CYCLOADDITION OF ALKENES, ALKINES AND  
DIENES WITH THE S-S-BOND OF  $[\text{Fe}(\text{CO})_3\text{S}]_2$

Ingo-Peter Lorenz and Anja Kramer

Institute for Inorganic Chemistry, University of Tübingen,

Auf der Morgenstelle 18, D-7400 Tübingen (FRG)

Organic and organometallic disulfides show a very similar reactivity; Seyferth et al. have proved this for reduction reactions of the disulfido cluster  $[(\text{CO})_3\text{FeS}]_2$  (1) into the corresponding dithiolate dianion  $[(\text{CO})_3\text{FeS}]_2^{2-}$ , which is a very useful synthon. Now, we succeeded in the photoinduced insertion reactions of alkenes, alkynes and dienes into the S-S-bond of 1, to obtain the corresponding 1,2-dithiolato complexes by 2+2-cycloadditions. Carbon monoxide and diazomethane are inserted by the carbon atom to give the bridging dithio-carbonato or methanedithiolato ligand, respectively. In one case the dithiolato ligand can be oxidized to the corresponding mixed sulfenatothiolato ligand:



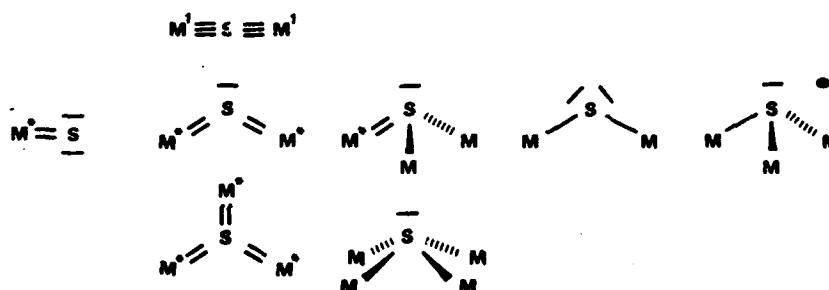
## NEUTRAL AND CATIONIC ORGANOMETALLIC SULFUR COMPLEXES

Ingo-Peter Lorenz, Guido Effinger and Andrea Spiesberger

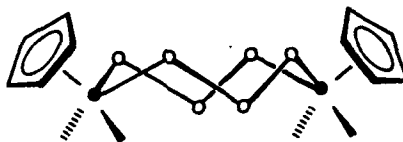
Institute for Inorganic Chemistry, University of Tübingen

Auf der Morgenstelle 18, D-7400 T ü b i n g e n (FRG)

Organometallic sulfur complexes and clusters play an important role as models for the active sites of redox enzymes and for the dehydrosulfurization catalysis. Sulfur demonstrates a great structural variety in metal-sulfur bonding (single, double and triple bonds) depending on the number of electrons of the organometallic complex fragment. Thus, sulfur can act as 2, 4 or 6 electron donor preferring bridging positions ( $\mu_2$ - $\mu_4$ -S):



Starting from the new sulfur sources thiirane,  $C_2H_4S$ , or bis(trimethylsilyl)sulfane,  $S(SiMe_3)_2$ , and suitable organometallic compounds, we succeeded in the syntheses of examples of some of the bonding systems introduced above, which are the isolobal analogues of sulfur dioxide, sulfanes, sulfoxides and sulfonium cations; a very interesting compound is obtained by the reaction of  $[Cp(CO)_2Mn]_2S$  with  $S_8$ :





INVESTIGATIONS OF HYPERVALENT TELLURIUM COMPOUNDS IN THE SOLID STATE AND IN SOLUTION

Dainis Dakternieks<sup>A</sup>, Robert Di Giacomo<sup>B</sup>, Robert W. Gable<sup>B</sup> and Bernard F. Hoskins<sup>B</sup>

<sup>A</sup> Division of Chemical and Physical Sciences, Deakin University, Geelong, Victoria 3217, Australia.

<sup>B</sup> Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.

Multinuclear magnetic resonance techniques and X-ray crystallography were used to investigate a series of organoyltellurium(IV) complexes in solution and in the solid state respectively. The X-ray crystal structures of the compounds  $C_8H_8Te(Etxan)_2$ ,  $C_8H_8Te(Etdtp)_2$ ,  $C_8H_8Te(Etdtc)_2$  and  $C_8H_8Te(I)(Etdtc)$  (where  $Etxan = S_2COEt$ ;  $Etdtp = S_2P(OEt)_2$ ;  $Etdtc = S_2CNET_2$  and  $C_8H_8 = o$ -xylene  $-\alpha,\alpha'$ -diyl) show that the tellurium atom is either seven or eight coordinate, with an active lone electron pair occupying an effective coordinate site in each case.

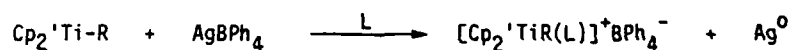
Carbon-13,  $^{31}P$  and  $^{125}Te$  NMR data indicate that intramolecular monodentate-bidentate dithiolate exchange becomes slow on the NMR time scale at low temperature and the structures inferred in solution approximate those observed directly in the solid state. Conformational isomers are observed in solutions of mixed-ligand complexes of the type  $C_8H_8Te(^1Prdtp)(Etdtp)$  and the distribution of these isomers is solvent dependent.

The complexes  $Ph_2Te(S-S)_2$  (where  $S-S =$  xanthate, dithiosphate, dithiocarbamate) are not as stable as their  $C_8H_8Te(S-S)_2$  analogues. NMR data indicate that in solution, these complexes rapidly disproportionate to  $Ph_2Te$  and the corresponding disulphide. Low temperature NMR studies of the dithiocarbamate complexes are in accord with a seven coordinate geometry about the tellurium atom, consistent with the structure determined in the solid state by X-ray crystallography.

NEW CATIONIC ALKYLBI(CYCLOPENTADIENYL)TITANIUM COMPLEXES  
BY ONE-ELECTRON OXIDATION OF Ti(III) ALKYL

Manfred Bochmann and Andrew J. Jaggar, School of Chemical Sciences,  
University of East Anglia, Norwich NR4 7TJ, U.K.

Cationic alkylbis(cyclopentadienyl)titanium complexes,  $[\text{Cp}_2\text{TiR(L)}]^+$ , are currently being discussed as intermediates in olefin polymerisation reactions based on  $\text{Cp}_2\text{TiCl}_2 / \text{AlR}_2\text{Cl}$  systems. While the synthesis of these complexes via substitution of  $\text{Cl}^-$  by L in  $\text{Cp}_2\text{Ti(R)Cl}$  is restricted to L being a good electron donor,<sup>1</sup> the one-electron oxidation of  $\text{Cp}_2'\text{TiR}$  ( $\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$ ) with  $\text{Ag}^+$  provides a generally applicable route. Complexes with labile L (e.g. L = THF) have now been obtained.



The cationic complexes react readily with CO, isocyanides and nitriles. The structure of  $[(\text{C}_5\text{Me}_5)_2\text{TiMe(THF)}]\text{BPh}_4$  has been determined by X-ray diffraction.<sup>2</sup>

- (1) M. Bochmann and L.M. Wilson, J. Chem. Soc., Chem. Commun. 1986, 1610;  
M. Bochmann, L.M. Wilson, M.B. Hursthouse and R.L. Short, Organometallics  
1987, 6, 2556.
- (2) M.B. Hursthouse and M. Motevalli, to be published.

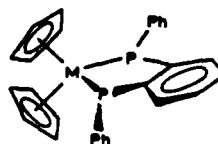
METALLOCENE *o*-PHENYLENEBIS(PHENYLPHOSPHANATO) CHELATES OF EARLY  
TRANSITION METALS

Hartmut Köpf and Verena Richterling, Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, Germany

*o*-Phenylenebis(phenylphosphane),  $o\text{-(PhHP)}_2\text{C}_6\text{H}_4$ , was deprotonated and was introduced as a dianionic, bidentate chelate ligand  $[o\text{-(PhP)}_2\text{C}_6\text{H}_4]^{2-}$  into the bent metallocene systems of early transition metals of subgroups IV or VI. Thus, the dilithium salt  $o\text{-(LiPhP)}_2\text{C}_6\text{H}_4$  reacted with equivalent amounts of metallocene dichlorides,  $\text{Cp}_2\text{MCl}_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), to give the new five-membered chelate complexes  $\text{Cp}_2\text{M(PPh)}_2\text{C}_6\text{H}_4\text{-}o$  ( $\text{M} = \text{Ti}$ , 1, green;  $\text{Zr}$ , 2, orange;  $\text{Hf}$ , 3, red;  $\text{Mo}$ , 4, brown;  $\text{W}$ , 5, ochre-yellow). Compounds 1-3 could be prepared more conveniently by reacting  $o\text{-(PhHP)}_2\text{C}_6\text{H}_4$  with equimolar amounts of the dimethylmetallocenes  $\text{Cp}_2\text{MMe}_2$  ( $\text{M} = \text{Ti}$ ,  $\text{Zr}$ ,  $\text{Hf}$ ). The  $^{31}\text{P}\{^1\text{H}\}$ -NMR-spectra of 1-5 each showed two singlets of different intensity due to the existence of trans (predominant) and cis isomers of the metallacycles in solution at room temperature.



cis-isomer



trans-isomer

# IONIC TITANOCENE COMPLEXES:

## A NEW TYPE OF ANTITUMOR CYCLOPENTADIENYL METAL COMPOUNDS

Petra Köpf-Maier, Institut für Anatomie, Freie Universität Berlin, Königin-Luise-Straße 15, D-1000 Berlin 33, Germany

Thomas Klapötke and Hartmut Köpf, Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, Germany

Bis( $\eta^5$ -cyclopentadienyl)titanium(IV) ("titanocene") diacido complexes  $(C_5H_5)_2TiX_2$  have proven to exhibit antitumor activity against diverse animal and human tumors. These compounds are neutral complexes containing two acido ligands X which are covalently bound to the central metal titanium. They are soluble in water to an only limited extent, thus requiring the addition of a solubilizer to the aqueous injection fluid when administered in higher dose levels.

In the present study, we investigated a new type of bis- and mono- ( $\eta^5$ -cyclopentadienyl)titanium(IV) complexes and report now upon antitumor properties of some ionic titanocene complexes, mainly represented by the acetonitrile complex  $[(C_5H_5)_2TiCl(NCCH_3)]^+[FeCl_4]^-$  (I), the 2,2'-bipyridyl derivative  $[(C_5H_5)_2Ti(bipy)]^{2+}[CF_3SO_3]_2^-$  (II), the N-methyl-o-aminothiophenolate complex  $[(C_5H_5)_2Ti(o-S(NHCH_3)C_6H_4)]^+I^-$  (III) and the five-coordinate bis(dithiolene) chelate  $[(C_5H_5)Ti(1,2,4-S_2C_6H_3CH_3)_2]^- [N(C_2H_5)_4]^+$  (IV).

I-III were tested against fluid Ehrlich ascites tumor growing in the peritoneal cavity of mice and effected optimum cure rates ranging between 70 and 100 % and therapeutic indices between 1.5 and 1.9. These values are similar to those caused by neutral titanocene dihalides and related compounds. As ionic titanocene complexes are distinguished by improved water solubility due to their salt-like character, they are obviously superior to neutral titanocene complexes with respect to biological application.

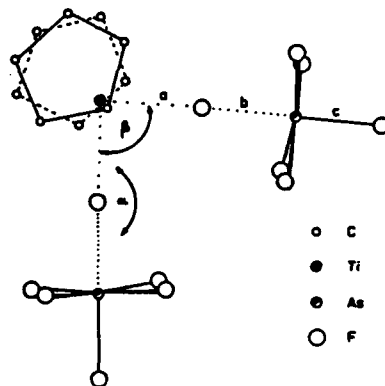
METALLOCENE CHEMISTRY OF HIGHLY FLUORINATED LIGAND SYSTEMS:  
TITANIUM(IV) CYCLOPENTADIENYL HEXAFLUOROPNICTOGENATES \*

Thomas Klapötke, Institut für Anorganische und Analytische Chemie der  
Technischen Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, FRG.

Ulf Thewalt, Sektion für Röntgen- und Elektronenbeugung der Universität Ulm,  
Oberer Eselsberg, D-7900 Ulm, FRG.

Transition metal halides have been reported to possess Lewis base qualities and it has been assumed that the metal-halide bond is not broken in the complexes formed. Adduct formation between  $\text{Cp}_2\text{TiF}_2$  and Lewis acids has been investigated. However, for a long time Lewis acid adducts of the type  $\text{Cp}_2\text{Ti}(\text{LF})_2$  ( $\text{L} = \text{BF}_3, \text{PF}_5$ ) were known to be unstable and not existent in the solid state.

In the present study, we investigated the reaction behaviour of  $\text{Cp}_2\text{TiF}_2$  toward the very powerful  $\text{F}^-$  acceptors  $\text{AsF}_5$  and  $\text{SbF}_5$ . The novel titanocene derivatives  $\text{Cp}_2\text{Ti}(\text{AsF}_6)_2$ ,  $\text{Cp}_2\text{Ti}(\text{SbF}_6)_2$ , and  $\text{Cp}_2\text{Ti}(\text{Sb}_2\text{F}_{11})_2$  have been prepared and were characterized by chemical analysis, IR, mass, and  $^1\text{H}$  NMR spectroscopy. More convenient these complexes are easily available by salt elimination reaction in  $\text{SO}_2$  from the corresponding silver hexafluoropnictogenates. Whereas these thermodynamically unstable titanocene compounds are kinetically stabilized the mono(cyclopentadienyl) species are kinetically unstable and decompose even at  $-50^\circ\text{C}$ . Reaction behaviour and mechanism of the decomposition reactions are discussed. Like the IR the single crystal X-ray structure of  $\text{Cp}_2\text{Ti}(\text{AsF}_6)_2$  shows a distorted  $\text{AsF}_6$  unit with fluorine co-ordinated (linear) to both, Ti and As:



\* Organo transition metal chemistry of highly fluorinated ligand systems (Organo-Übergangsmetall-Chemie hochfluorierter Ligand-Systeme): 5th communication.

Cyclopentadienyl(2,2-bipyridyl) complexes of titanium,  
zirconium, niobium

O.N.Suvorova, V.V.Kutyryova, N.B.Patrikeeva, G.A.Domrachev  
Institute of Chemistry, Academy of Sciences of USSR, Gorky

The aim of this work is the investigation of thermal decomposition of the cyclopentadienyl(2,2-bipyridyl) titanium, zirconium, niobium complexes and formation of the films of inorganic materials in conditions of gas-phase precipitation.

The starting compounds  $\text{CpTi}(\text{bipy})$ ,  $\text{Cp}_2\text{Zr}(\text{bipy})$ ,  $\text{Cp}_2\text{Nb}(\text{bipy})$  have been prepared by the reaction of  $\text{Li}_2(\text{bipy})$  with  $\text{Cp}_2\text{MCl}_2$ .

All complexes are crystal substances of deep-blue or black colour, extreme easily reacting with oxygen of air, therefore all operations with them have been carried out in atmosphere of argon and in vacuum. Spectral characteristics of this compounds have been obtained.

The thermographic investigations of thermal decomposition of all studied compounds are carried out. The volume of evolved gaseous products of decomposition was fixed simultaneously with the registration of DTA curves. The thermal decomposition of homoleptic bipyridyl complexes  $\text{Ti}(\text{bipy})_3$  and  $\text{Nb}(\text{bipy})_3$ , dicyclopentadienyl compounds  $\text{Cp}_2\text{MCl}_2$  and mixed cyclopentadienylchelate compounds such as  $\text{CpMCh}_2\text{Cl}$ ,  $\text{ChM}(\text{bipy})$  have been investigated for comparison of reaction directions and conditions.

The influence of the structure of initial compounds on composition and structure of inorganic materials films, on conditions of their formation and properties has been shown.

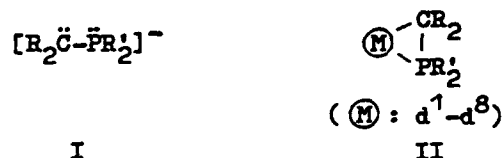
Some ferrocenyl chelate complexes of transition metals of the type of  $\text{Fc}_2\text{MCh}$ ,  $\text{Fc}_2\text{M}(\text{bipy})$  have been prepared in this work.

$\eta^1$ - VERSUS  $\eta^2$ -COORDINATION IN PHOSPHINOMETHYL ZIRCONIUM COMPLEXES

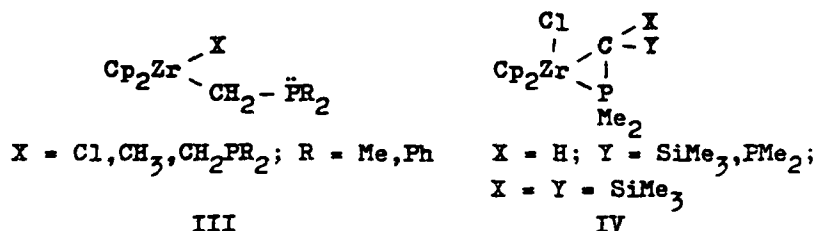
Hans H. Karsch, B. Deubelly, G. Müller

Anorganisch-chemisches Institut, Technische Universität München,  
Lichtenbergstr. 4, D-8046 Garching, F.R.G.

Due to the ambidentate nature of phosphinomethanides I,



unsaturated metal complexes form three membered rings II in most cases.

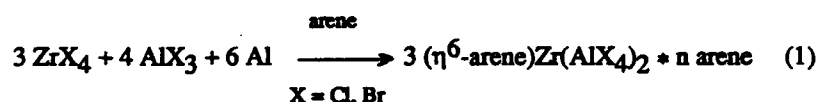
Computational studies predict  $\eta^2$ -coordination also for the  $d^0$ -complex  $\text{Cp}_2\text{Zr}(\text{Cl})\text{CH}_2\text{PR}_2^1$ , but all (real) complexes III of this type, studied so far, exhibit  $\eta^1$ -coordination<sup>2</sup>.According to our structural findings on lithium derivatives of I, P-coordination of I is supported by silyl or phosphino substituents at the carbanion ( $\text{R} = \text{SiMe}_3, \text{FMe}_2$ ). In fact, complexes IV exhibit  $\eta^2$ -coordination in the solid state. Hence, comparing III and IV, the coordination number of zirconium increases on enhancing the size of the ligand. Preparation, structures and properties of these and related compounds are discussed.

- 1) Hofmann, P.; Stauffert, P.; Shore, N.E. Chem. Ber. 1982, 115, 2153.
- 2) Karsch, H.H.; Müller, G.; Krüger, C. J. Organomet. Chem. 1984, 273, 195. - Young, S.J.; Olmstead, M.M.; Knudsen, M.J.; Shore, N.E. Organometallics 1985, 4, 1432.

### Arene derivatives of zirconium(II)

Fausto Calderazzo, Guido Pampaloni and Piersandro Pallavicini, Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Via Risorgimento 35, I-56100 Pisa, Italy.

The chemistry of low-valent Group 4 transition elements (oxidation state less than III) is still largely unexplored, especially when the non-cyclopentadienyl organometallic derivatives of these elements are concerned <sup>1</sup>. In the framework of our studies on the synthesis and properties of low-valent early transition metal derivatives <sup>2</sup>, we have found that the reaction of the tetrahalides of zirconium(IV),  $ZrX_4$ , with  $Al/AlX_3$  in arene as solvent proceeds according to equation (1) and the products were isolated and/or characterized spectroscopically.



A new preparation of the zirconium and hafnium tetrabromide and tetraiodide was found by reacting  $M(BH_4)_4$  and anhydrous  $HX$  in n-heptane as solvent, according to equation (2):



Work is in progress in order to extend these reactions to hafnium and to study the reactivity of such systems towards  $CO$ ,  $CO_2$ , olefins, alkynes.

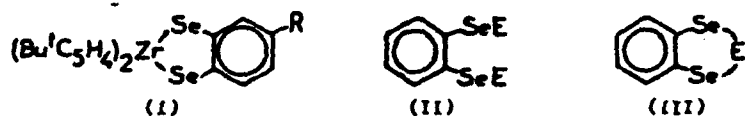
Financial support from ENICHEM ANIC, Milano, is gratefully acknowledged.

- 1 M. Bottrill, P.D. Gravens and J. McMeeking in "Comprehensive Organometallic Chemistry", G. Wilkinson, F.G.A. Stone and E.W. Abel, Eds., Pergamon Press, Oxford, 3, 281 (1982); D.J. Cardin, M.F. Lappert and C.L. Raston, Chemistry of Organo-Zirconium and Organo-Hafnium Compounds, Ellis Horwood, 1986.
- 2 P. Biagini, F. Calderazzo, G. Pampaloni and P.F. Zanazzi, Gazz. Chim. Ital., 117, 27 (1987); P. Biagini, F. Calderazzo and G. Pampaloni, J. Chem. Soc., Chem. Commun, 1015 (1987).



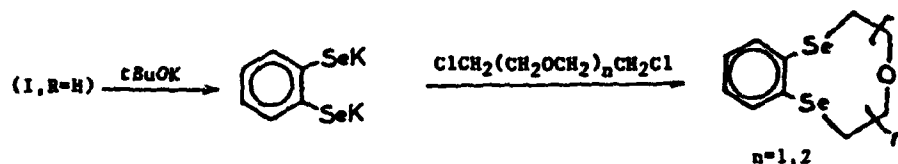
Philippe Meunier, Bernard Gautheron, Jacques Bodiguel and Pascale Tavarès  
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS  
(UA 33), Faculté des Sciences, 6 bd Gabriel 21000 Dijon (France)

Recently we have shown that electrophiles  $EC1$  and  $EC1_2$  react easily with diselenophenylene zirconocene (I) leading to various diseleno aromatic compounds (II, III) (1,2).

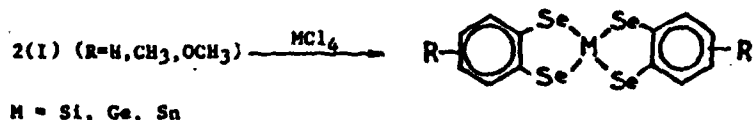


We are presently reporting new applications of complex I.

#### 1) Synthesis of first Se-containing crown ethers



#### 2) Formation of new silicon, germanium and tin spiro derivatives



All compounds were characterized by  $^1H$  NMR and mass spectrometry.

#### References

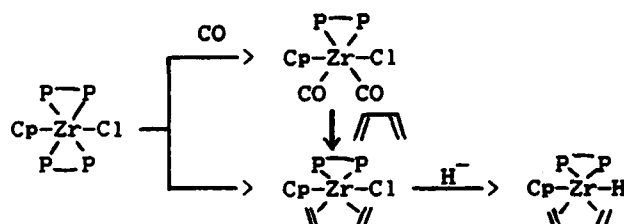
1. P. Meunier, B. Gautheron and A. Mazouz, J. Chem. Soc., Chem. Comm., 1986, 424.
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Low-valent monocyclopentadienyl zirconium chemistry: synthesis, structure and reactivity.

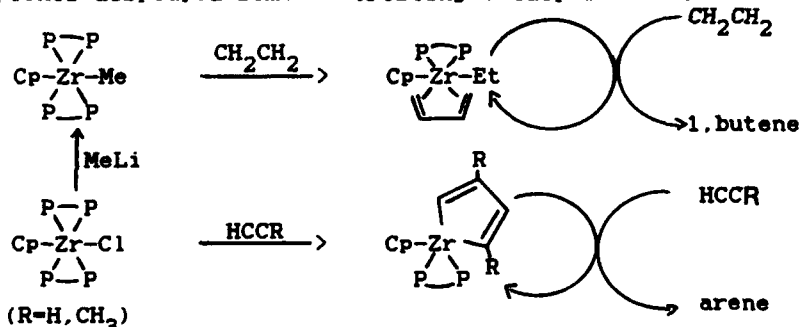
Sandro Gambarotta, Ytsen Wielstra. Laboratorium voor Anorganische Chemie, Rijksuniversiteit Groningen, Nijenborgh 16 9747AG Groningen, The Netherlands

Michael Y. Chiang, Chemistry Department, Columbia University, New York, N.Y. 10027, USA

Apart from the bis(cyclopentadienyl) systems, very little is known in the chemistry of low-valent zirconium (1). We found that  $\text{CpZr}(\text{dmpe})_2\text{Cl}$  (2) is a versatile synthetic tool to enter this chemistry. Mild condition reaction with unsaturated substrates in fact, allowed the easy substitution of one phosphine ligand and the preparation of new compounds including halocarbonyls and diene derivatives. The structures of all the complexes have been demonstrated by X-ray analysis



Chlorine replacement has been achieved by reaction with MeLi forming the first low-valent zirconium-alkyl. Preliminary results on the reactivity of these species with light olefins and acetylenes displayed some interesting catalytic features.



For example, reaction of  $\text{CpZr}(\text{dmpe})_2\text{Me}$  with 3 equivalents of ethylene led to the formation of  $\text{CpZr}(\text{dmpe})(\text{diene})\text{Et}$  which selectively catalyzed the dimerization of ethylene to 1-butene. Catalytic cyclotrimerization has been obtained instead with propyne and acetylene. The catalytic species have been fully characterized including by X-ray analysis.

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- 1) Lappert, M.F. Chemistry of organo zirconium and hafnium compounds Ellis Horwood 1984
- 2) Gambarotta, S.; Chiang, M.Y. J.Chem.Soc.Chem.Comm.1987,698

Synthesis and structural studies of mono- and bis-( $\eta^5$ -cyclopentadienyl)hafnium(IV) derivatives of heterocyclic thioketones

O.P. Pandey, Organometallic Research Laboratory, Department of Chemistry, University of Gorakhpur, Gorakhpur 273009, India

The reactions of dichlorobis( $\eta^5$ -cyclopentadienyl)hafnium(IV) with four different classes of heterocyclic thioketones viz., 3-substituted-4-amino-s-triazole-5-thiol, 1-substituted-2-thiohydantoin, 5-substituted 1,3,4-oxadiazole-2-thione and 1-substituted tetrazoline-5-thione were studied in anhydrous tetrahydrofuran in the presence of base. The reaction products were characterized on the basis of elemental analyses, electrical conductance, magnetic susceptibility and spectral (electronic, infrared and  $^1\text{H}$ .m.r.) data.

$^1\text{H}$  AND  $^{13}\text{C}$  NMR SPECTRAL STUDIES ON ORGANO-RHODIUM(I)  
COMPLEXES CONTAINING NITROGEN HETEROCYCLES.

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Bangalore University, Bangalore-560 001, India.

ABSTRACT

The chlorobridged binuclear complex,  $[\text{Rh Cl (DCPD)}]_2^1$  containing the tricyclic diolefin, *endo*-dicyclopentadiene (DCPD) reacts with exobidentate nitrogen heterocycles (N-N) in acetone to yield (N-N)- bridged complexes of the type  $[(\text{DCPD})(\text{Cl})\text{Rh}(\text{N-N}) \text{ Rh}(\text{Cl})(\text{DCPD})]$ , where N-N is 4,4' bipyridyl, pyrazine or *trans*- 1, 2 - Bis (4-Pyridyl) ethylene. The chlorobridged binuclear complex also reacts with 2-substituted benzimidazole derivatives (R-BztH; R = H, Me, Et, n-Pr) to produce polynuclear complexes  $[\text{Rh (DCPD)-(R-Bzt)}]_n$ . Several of these complexes have been investigated by  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra, in addition to physico-chemical measurements. In the case of DCPD and  $\text{Rh}_2\text{Cl}_2 (\text{DCPD})_2$ , the pmr spectral assignments have been further corroborated by 2-D and 1-D difference NOE (Nuclear Overhauser Effect) nmr spectral studies

REFERENCE

- <sup>1</sup>J. Chatt and L.M. Venanzi J. Chem. Soc. (1957) 4735-40.

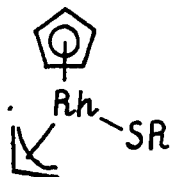
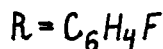
## 4-FLUOROTHIOPHENOLATE DERIVATIVES OF RHODIUM

Z.I. Iutsenko, E.M. Rokhlina, A.S. Peregudov, A.Z. Rubezhov,  
D.N. Kravtsov

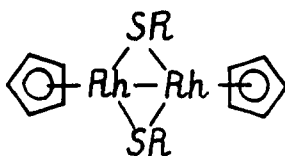
A.N. Nesmeyanov Institute of Organoelement Compounds, U.S.S.R.  
Academy of Sciences, 28 Vavilov Str., Moscow 117813, U.S.S.R.

With the exception of rhodanides, no metal-sulphur bonded  $\pi$ -Allyl- $\pi$ -Cp and  $\pi$ -Allyl- $\pi$ -Arene complexes of Rh and Ru appear to be known. In view of the studies on relative polarity and reactivity of transition metal-sulphur bonds, the corresponding thiophenolates are of interest. In this connection, interaction of  $\pi$ -C<sub>3</sub>H<sub>5</sub>- $\pi$ -C<sub>5</sub>H<sub>5</sub>RhCl (I) and  $\pi$ -C<sub>3</sub>H<sub>5</sub>- $\pi$ -C<sub>6</sub>H<sub>6</sub>RuCl (II) with 4-fluorothiophenol and its derivatives has been examined.

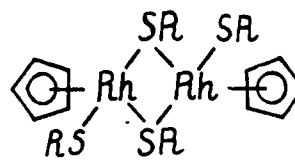
Reaction of I with 4-FC<sub>6</sub>H<sub>4</sub>SH in the presence of excess triethylamine leads to a mixture of complexes III, IV and V:



III



IV



V

The structures of products obtained were based on <sup>1</sup>H, <sup>19</sup>F NMR and mass-spectroscopic data.

Under the same conditions, II does not react with 4-FC<sub>6</sub>H<sub>4</sub>SH. All attempts to obtain  $\pi$ -C<sub>3</sub>H<sub>5</sub>- $\pi$ -C<sub>6</sub>H<sub>6</sub>RuSC<sub>6</sub>H<sub>4</sub>F by reactions of II with 4-FC<sub>6</sub>H<sub>4</sub>SM (M=Na, Ag) or 4-FC<sub>6</sub>H<sub>4</sub>SH in the presence of AgBF<sub>4</sub> met with little success.

STABLE PARAMAGNETIC PLATINUM GROUP METAL HYDRIDES: SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND BEHAVIOR IN SOLUTION OF THE COMPLEX  $\text{Rh(IV)(H)}_2(\text{Cl})_2(\text{P-}i\text{-Pr}_3)_2$ , 1.

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D. Attanasio, Istituto di Teoria e Struttura e Comportamento Spettrochimico dei Composti di Coordinazione, Area della Ricerca di Roma - C.N.R. - 00016 Monterotondo Stazione - Roma - Italy.

Recently we reported the synthesis, x-ray crystal structure and behavior in solution of the first two examples of stable paramagnetic platinum group metal hydrides: the complexes  $\text{Ir(IV)(H)}_2(\text{Cl})_2(\text{P-}i\text{-Pr}_3)_2$  and  $\text{Ir(IV)(H)}_2(\text{Cl})_2(\text{PCy}_3)_2$ <sup>1-3</sup>. Considering the stability of these compounds we thought that rhodium, like iridium, should give stable paramagnetic hydrides. Indeed we have synthesized the stable paramagnetic complex  $\text{Rh(IV)(H)}_2(\text{Cl})_2(\text{P-}i\text{-Pr}_3)_2$ , 1, which shows to be isomorphous with the iridium compound<sup>1</sup>.

Paramagnetic rhodium (IV) complexes are very rare, the only well-defined species are the two cesium salts  $\text{Cs}_2\text{RhCl}_6$  and  $\text{Cs}_2\text{RhF}_6$ . To our knowledge, compound 1 is the first example of a stable paramagnetic hydride of rhodium (IV).

In this work we present synthesis, x-ray crystal structure, magnetic properties both in the solid state and in solution, and NMR in solution of compound 1.

1) P. Mura J. Am. Chem. Soc. 1986, 108, 351-352.

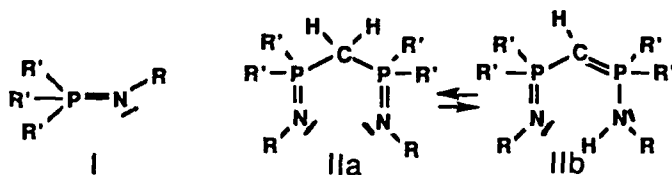
2) P. Mura and A. Segre Angew. Chemie, 1986, 25, 460-462.

3) P. Mura, A. Segre and S. Sostero, submitted to J. Am. Chem. Soc.

**The coordination and organometallic chemistry of bis(iminophosphoranyl)methane with rhodium complexes.**

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Laboratory of Inorganic Chemistry, University of Amsterdam,  
Nieuwe Achtergracht 166, 1018WV Amsterdam.

The organometallic and coordination chemistry of dienes containing several hetero atoms continues to be of interest. One of our current research items comprises a study of the coordination and reactivity of phosphinimides (I) and bis(iminophosphoranyl)methane (IIa) with  $d^8$  transition metal complexes.



Bis(iminophosphoranyl)methane may, in analogy to bis(methylenephosphoranyl)methane (1), exist as 2 isomers (IIa and IIb). However isomer IIa appears to be the groundstate in solution as well as in the solid state. When bis(N-p-tolyl-imino-P,P-diphenylphosphoranyl)methane (IIa, R=p-tolyl, R'=Ph) is reacted with Rh(I) compounds two different coordination complexes are formed: i.e. N-N and N-C coordination to Rh (X-Ray) occurs. These coordination modes can be regarded as the Rh stabilized forms of IIa and IIb respectively (R=p-tolyl, R'=Ph).

The coordination and organometallic chemistry of bis(iminophosphoranyl)methane with Rh(I) and the reactivity of the Rh complexes towards small molecules will be discussed.

1. R.Appel, G.Haubrich, F.Knoch; Chem.Ber. 117(1984)2063

SYNTHESIS, STRUCTURE AND CHEMICAL PROPERTIES OF SOME  
 $\eta^4$ -TRICARBONYLCHROMIUM- $\eta^3$ -(CYCLOOCTADIENE)RHODIUM INDENYLS.

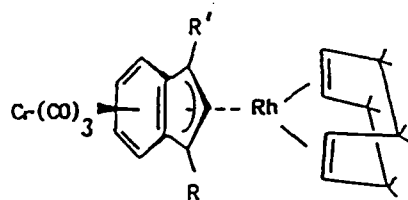
Alberto Ceccon, Alessandro Gambaro, Saverio Santi  
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Transition metal indenyl complexes often exhibit higher reactivity than the iso-structural cyclopentadienyl derivatives. Usually, indenyl ligand is bonded to the metal via the C<sub>8</sub>-ring and, unlike the cyclopentadienyl analog, it may undergo a facile bonding transformation from a penta-hapto to a tri-hapto coordinative mode.<sup>1</sup>

We have prepared some indene bimetallic complexes by quenching the appropriate  $\eta^4$ -Cr(CO)<sub>3</sub>-indenyl anion with (RhClCOD)<sub>2</sub> (COD  $\equiv$  1,5-cyclooctadiene):



- |     |                                   |                                    |
|-----|-----------------------------------|------------------------------------|
| I   | R = H                             | R' = H                             |
| II  | R = H                             | R' = CH <sub>3</sub>               |
| III | R = CH <sub>3</sub>               | R' = CH <sub>3</sub>               |
| IV  | R = H                             | R' = C <sub>6</sub> H <sub>5</sub> |
| V   | R = C <sub>6</sub> H <sub>5</sub> | R' = C <sub>6</sub> H <sub>5</sub> |

Structural assignments based on X-ray and NMR spectra of the compounds will be presented.

The activity of these bimetallic species as catalysts will be compared with that of the parent ( $\eta^3$ -indenyl)-Rh-COD complex.

<sup>1</sup> J.M.O'Connor, C.P.Casey, Chem. Rev., **87** (1987) 307.

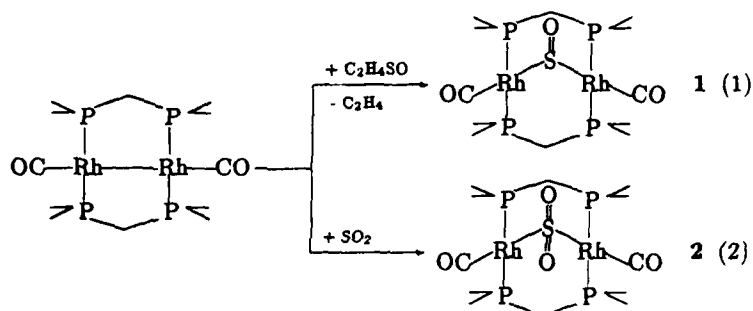


# NEW SULFUR MONOXIDE AND SULFUR DIOXIDE COMPLEXES OF RHODIUM AND PLATINUM

Ingo-Peter Lorenz and Armin Neher

Universität Tübingen, Institut für Anorganische Chemie,  
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The reaction of thiirane S-oxide with the dimeric  $[\text{Rh}(\text{CO})(\mu\text{-dppm})]_2$  [dppm=bis(diphenylphosphino)methane] results in the new SO-complex  $[\text{Rh}_2(\mu\text{-SO})(\text{CO})_2(\mu\text{-dppm})_2]$  **1** with A-frame type structure and a bridging SO-group as 3c2e-system. The analogous reaction with  $\text{SO}_2$  yields the new sulfur dioxide complex  $[\text{Rh}_2(\mu\text{-SO}_2)(\text{CO})_2(\mu\text{-dppm})_2]$  **2** of the same type, eq 1 and 2:



These A-frame complexes have been characterized by  $^{31}\text{P}\{^1\text{H}\}$  NMR, IR and mass-spectroscopy (FAB). The AA'BB'XX'- and AA'A''A'''XX'-  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **1** and **2**, respectively, were resolved by 2D-COSY-NMR experiments and simulation.

Reaction of the dimeric platinum complex  $[\text{PtCl}(\mu\text{-dppm})]_2$  with thiirane S-oxide results in the  $\text{SO}_2$ -A-frame complex. This reaction shows, that if 'SO', generated from thiirane S-oxide, can't be stabilized in the coordination sphere of a metal complex, it will decompose into sulfur and sulfur dioxide.

A monomer sulfur monoxide complex with terminal SO-group has been prepared by the reaction of thiirane S-oxide with  $[\text{Rh}(\text{dppm})_2]\text{PF}_6$ , eq 3.



**3** has been characterized by  $^{31}\text{P}\{^1\text{H}\}$  NMR, IR and mass-spectroscopy (FAB), too.

INTRAMOLECULAR 1,2-HAPTOTROPIC SHIFT IN SQUARE-PLANAR COMPLEXES  
OF NICKEL (II) WITH PYRIDAZINE.

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Inorgànica, Facultat de Química, Universitat de Barcelona,  
08028-Barcelona, Spain.

The square-planar complexes  $[\text{Ni}(\text{pdz})\text{R}(\text{PR}'_3)_2]^+$  (pdz= pyridazine;  
 $(\text{PR}'_3)_2$ = 1,2-bis(diphenylphosphino)ethane, R=  $\text{C}_6\text{Cl}_5$ ,  $\text{C}_6\text{F}_5$ , 2,3-  
 $\text{C}_6\text{H}_3\text{Cl}_2$ ;  $\text{PR}'_3$ =  $\text{PEt}_3$ , R=  $\text{C}_6\text{Cl}_5$ ) have been prepared by the  
reaction of  $[\text{Ni}(\text{acetone})\text{R}(\text{PR}'_3)_2]^+$  prepared "in situ" from  
 $[\text{NiXR}(\text{PR}'_3)_2]$  (X= Cl, or Br) and  $\text{AgClO}_4$ , with the amine.

The variable temperature  $^1\text{H}$  NMR studies of these complexes have  
shown that at low temperature they are monomers with the pdz  
ligand bound through only one nitrogen atom, and that at high  
temperature they are fluxional species in which there is a rapid  
exchange of the site of nickel coordination between the two  
nitrogen atoms of the monodentate pyridazine. The mechanism for  
this 1,2-haptotropic shift is, apparently, intramolecular. The  
energy barrier for this exchange has been found to depend on the  
trans effect of the ligand trans to the amine. In the presence  
of free pdz another exchange process between free and  
coordinated ligand has been observed for the less sterically  
crowded complexes (R=  $\text{C}_6\text{F}_5$ , and 2,3- $\text{C}_6\text{H}_3\text{Cl}_2$ ), the process  
occurring at temperatures higher than those of the 1,2-  
haptotropic shift.

## NEW HYDROXO-BRIDGED COMPLEXES OF THE NICKEL GROUP ELEMENTS

Gregorio López, Gabriel García, José Ruiz, Gregorio Sánchez, Joaquín García and Juan J. Ponti

Departamento de Química Inorgánica, Universidadde Murcia, Santo Cristo 1, 30001-Murcia, Spain

Hydroxo-complexes of the later transition metals are of interest because their potential reactivity promises extensive utility in organic and organo-metallic synthesis. Although some hydroxo-complexes of the nickel group elements have been described in the literature,<sup>1-4</sup> we have found that binuclear anionic complexes of the type  $[(C_6F_5)_2M(\mu-OH)_2M(C_6F_5)_2]^{2-}$  ( $M = Ni, Pd$ ) can be prepared by reaction of  $cis-M(C_6F_5)_2(PhCN)_2$  with  $(NBu_4)OH$ . Addition of  $HX$  to the di- $\mu$ -hydroxo-metallate(II) leads to the formation of the complexes  $[(C_6F_5)_2M(\mu-OH)-(\mu-X)M(C_6F_5)_2]^{2-}$  and  $[(C_6F_5)_2M(\mu-X)_2M(C_6F_5)_2]^{2-}$ ,  $X$  being anionic groups such as pyrazolate exobidentate ligands. Preliminary results indicate that platinum may exhibit a similar behaviour.

The new compounds have been characterized by microanalyses, conductivities and IR,  $^1H$ - and  $^{19}F$ -NMR spectroscopies.

A study of the reactivity of the di- $\mu$ -hydroxo-complexes towards organic compounds containing active methyl or methylene groups (acetone, nitromethane, malononitrile, ...) is now in progress.

## References

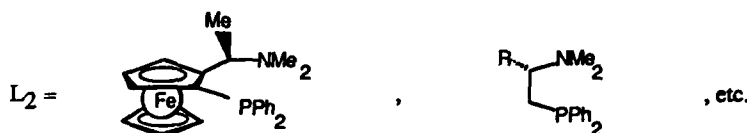
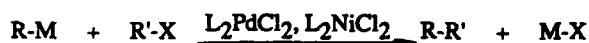
- (1) Carmona, E.; Marín, J.M.; Paneque, M.; Poveda, M.L. Organometallics 1987, **6**, 1757.
- (2) Yoshida, T.; Okano, T.; Otsuka, S. J. Chem. Soc., Dalton Trans. 1976, 993.
- (3) Appleton, T.G.; Bennett, M.A. Inorg. Chem. 1978, **17**, 738.
- (4) Ros, R.; Michelin, R.A.; Bataillar, R.; Roulet, R. J. Organomet. Chem. 1978, **161**, 75.

# Comparative reactivity of dimethylpalladium complexes with diphosphine, phosphino-amine, and diamine bidentate ligands<sup>1</sup>

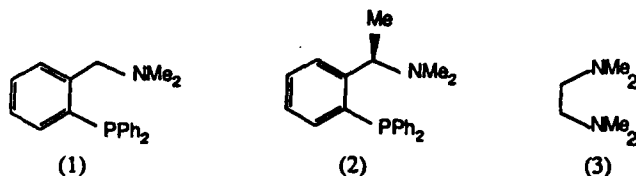
W. de Graaf, J. Boersma, and G. van Koten

University of Utrecht, Laboratory for Organic Chemistry, Dept. of Metal-Mediated Synthesis, Padualaan 8, 3584 CH Utrecht, The Netherlands

Many chiral ligands used in palladium- and nickel-catalyzed asymmetric coupling reactions contain both a phosphorus and a nitrogen donor atom.<sup>2</sup>



In these reactions, the last step is generally accepted to be reductive elimination of R-R' from a diorganopalladium species. We have investigated the effects of variation of the donor ligands on the mechanism of this reductive elimination in complexes of the type  $R_2PdL_2$ . To that end we have prepared and studied the reactivity of dimethylpalladium complexes with the P,N and N,N bidentate ligands *o*-diphenylphosphino-N,N-dimethylbenzylamine (1),<sup>3</sup> *o*-diphenylphosphino- $\alpha$ -methyl-N,N-dimethylbenzylamine (2),<sup>3</sup> and with N,N,N',N'-tetramethylethylenediamine (TMEDA):



## References

- 1 Part of this work has been published in preliminary form:  
W. de Graaf, J. Boersma, D.M. Grove, A.L. Spek and G. van Koten, *Recl. Trav. Chim. Pays-Bas* **107**, 299 (1988)
- 2 M. Kumada, *Pure and Appl. Chem.* **52**, 669 (1980); T. Hayashi and M. Kumada, *Acc. Chem. Res.* **15**, 395 (1982)
- 3 T. H. Rauchfuss, F. T. Patino and D. M. Roundhill, *Inorg. Chem.* **14**, 652 (1975)

"Pd(C<sub>6</sub>F<sub>5</sub>)Br", A CONVENIENT PRECURSOR FOR STUDYING THE NUCLEOPHILIC ENDO  
 ATTACK TO COORDINATED DIENES. X-RAY STRUCTURE OF  
 $[\text{Pd}_2(\mu\text{-Br})_2(1\text{-}3\text{-}\eta\text{-}4(\text{C}_6\text{F}_5)\text{cyclohexenyl})_2]$ .

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 Universidad de Valladolid, 47005 Valladolid, Spain.

C. Foces-Foces and F.H. Cano, Departamento de Rayos X, Instituto  
 Rocasolano, C.S.I.C., Serrano 119, 28006 Madrid, Spain.

Exo nucleophilic attack to dienes coordinated to Pd has been widely studied, but endo attack from nucleophiles attached to Pd has been less accessible to study and mostly limited to: a) addition of diolefins to  $[\text{PdHL}_2]^+$ , where the nucleophile  $\text{H}^-$  is undoubtedly attached to Pd but cannot be recognized after the formation of the  $\eta^3$ -allyl complex; and b) one-pot reactions of  $\text{Li}_2\text{PdCl}_4$  + diene +  $\text{RHgX}$  where an intermediate "PdRX" is likely to be formed but no direct evidence of its participation is available.

Our work is concerned with the reactions of  $[\text{Pd}(\text{C}_6\text{F}_5)\text{Br}(\text{S})_2]$  (S=solvent) with acyclic, cyclic, conjugated or non-conjugated diolefins to give, generally, allylic complexes of palladium. The advantages of using this "Pd(C<sub>6</sub>F<sub>5</sub>)Br" synthon are that: a) there is no doubt that the nucleophile, C<sub>6</sub>F<sub>5</sub>, is initially attached to the Pd atom; b) the C<sub>6</sub>F<sub>5</sub> group gives excellent information from IR and <sup>19</sup>F NMR spectroscopies; and c) the position of the attack can be determined from examination of the products.

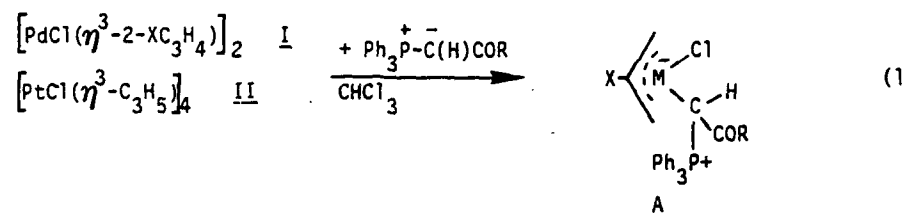
The results of the reactions with several diolefins as interpreted from <sup>1</sup>H and <sup>19</sup>F NMR spectroscopies and from the X-ray structure of  $[\text{Pd}_2(\mu\text{-Br})_2(1\text{-}3\text{-}\eta\text{-}4(\text{C}_6\text{F}_5)\text{cyclohexenyl})_2]$  will be presented.

## COORDINATION OF KETO-STABILIZED YLIDES ON Pd(II) AND Pt(II) SUBSTRATES

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Centro di Chimica Metallorganica, C.N.R. , Istituto di Chimica Industriale  
Facolta' di Ingegneria, Universita' di Padova, 35100 Padova, Italy

Ylides are electron donor ligands and react with metallic substrates [1] giving metal-carbon  $\sigma$ -bonds having surprising thermal and chemical stability. However electronic and steric factors of the organometallic framework and of the organic ylide can affect stability of the M-C(ylide) bond and the coordination mode of the ylide to the metal centre. We recently prepared Pd(II) and Pt(II) complexes with keto-stabilized ylides starting from dimers I and tetramer II, respectively [2]



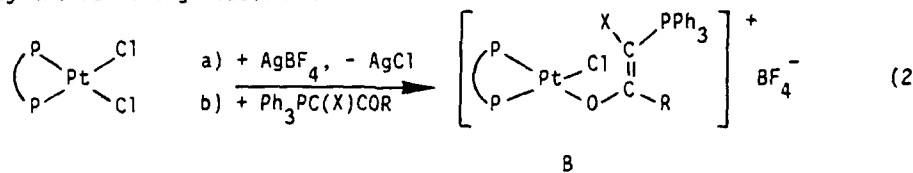
M=Pd; X=H, Me; R=Me, Ph;

M=Pt; X=H; R=Me, Ph, OMe

Compounds A show a labile M-C(ylide)  $\sigma$ -bond. The Pd(II) derivatives spontaneously dissociate in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$  giving rise to an equilibrium with starting

reagents. Substitution in complexes A of the  $\text{Cl}^-$  with a neutral  $\pi$ -accepting ligands (CNR) lightly stabilizes the  $\sigma$ -bond.

Keto-stabilized ylides can delocalize the negative charge of the carbonyl oxygen; so, in some cases, their coordination to the metal centre through the oxygen atom is possible. Complexes with Pt-O(ylide) bond have been obtained by the following reaction:


 $\text{P} \text{---} \text{P} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ; X=H, Br; R=CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>
 $\text{P} \text{---} \text{P} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ; X=CH<sub>3</sub>; R=C<sub>6</sub>H<sub>5</sub>

The nature of R moiety on the carbonyl group of ylides plays an important role in the coordination mode in the reaction (2).

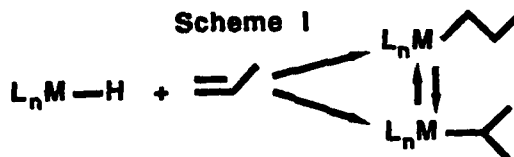
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ALKYL ISOMERIZATION STUDIES WITH NEW  
ALKYLPLATINUM (II) COMPLEXES

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Many important processes that are catalyzed by metal complexes involve the formation of hydridometal intermediates that react with alkenes to form alkylmetal complexes. As shown in Scheme I for propene, with most alkenes a number of alkylmetal isomers that are frequently in equilibrium form in this step. There has only been limited study of the factors that determine the position of this equilibrium.



A series of new alkyl complexes of platinum (II) has been prepared to study these factors in detail. Stable alkylmetal complexes of the type (ligand) $Pt(PR_3)(alkyl)$  (ligand = bischelate, monoanionic ligand) undergo alkylisomerization reactions (*e.g.* *sec*butyl  $\rightleftharpoons$  *n*-butyl) at elevated temperatures. Results on the relative stability of various alkylmetal isomers will be reported as well as mechanistic information on these isomerization reactions.

SYNTHESES AND STRUCTURES OF 2-DIPHENYLPHOSPHINOMETHYLENIDE-6-DIPHENYLPHOSPHINOMETHYLENEPYRIDINE COMPLEXES OF PALLADIUM(II) AND PLATINUM(II): CRYSTAL STRUCTURES OF  $[\text{PtCl}(2-(\text{CHPPH}_2)-6-(\text{CH}_2\text{PPh}_2)\text{PYRIDINE})]$  AND  $[\text{Pd}(\text{COOCH}_3)(2-(\text{CHPPH}_2)-6-(\text{CH}_2\text{PPh}_2)\text{PYRIDINE})]$ .

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#### Summary

The reactivity of the palladium(II) and platinum(II) complexes of formula  $\text{M}(\text{pnp})\text{Cl}_2$  ( $\text{M} = \text{Pd}, \text{Pt}$ ;  $\text{pnp} = 2,6\text{-bis}(\text{diphenylphosphinomethyl})\text{pyridine}$ ) and  $\text{Pt}(\text{dppf})\text{Cl}_2$  ( $\text{dppf} = 1,1'\text{-bis}(\text{diphenylphosphinomethyl})\text{ferrocene}$ ) in methanol solution with sodium methoxide under carbon monoxide atmosphere at room temperature and atmospheric pressure has been investigated.

In contrast with the behavior of the  $\text{Pt}(\text{dppf})\text{Cl}_2$  complex, which gives the corresponding bis-methoxycarbonyl compound, the terdentate ligand  $\text{pnp}$  of the  $\text{M}(\text{pnp})\text{Cl}_2$  complexes undergoes a nucleophilic attack by the methoxide ion, losing a proton and yielding complexes of formula  $\text{MX}[\text{C}_5\text{H}_3\text{N}(\text{CHPPH}_2)(\text{CH}_2\text{PPh}_2)]$  ( $\text{M} = \text{Pt}$ ,  $\text{X} = \text{Cl}, \text{COOCH}_3$ ;  $\text{M} = \text{Pd}$ ,  $\text{X} = \text{COOCH}_3$ ), which have been characterized by chemical and spectroscopic means. The crystal structures of  $\text{PtCl}(2-(\text{CHPPH}_2)-6-(\text{CH}_2\text{PPh}_2)\text{pyridine})$  (1) and  $\text{Pd}(\text{COOCH}_3)(2-(\text{CHPPH}_2)-6-(\text{CH}_2\text{PPh}_2)\text{pyridine})$  (2) have been determined by X-ray methods. Both structures were solved from diffractometric data by Patterson and Fourier techniques and refined by full-matrix least-squares to  $R = 0.0418$  (3338 observed reflections) for 1 and to  $R = 0.0663$  (3088 observed reflections) for 2. In both complexes the terdentate anionic ligand chelates the metal forming two five-membered rings, and the range for P-C and C-C bond lengths in one of the chelate rings is in agreement with a  $\text{sp}^2$  hybridization of the formally anionic methylenidic carbon and with a large delocalization in the ring.



A Possible Example of an Intramolecular Oxidative Addition - Reductive Elimination Process.

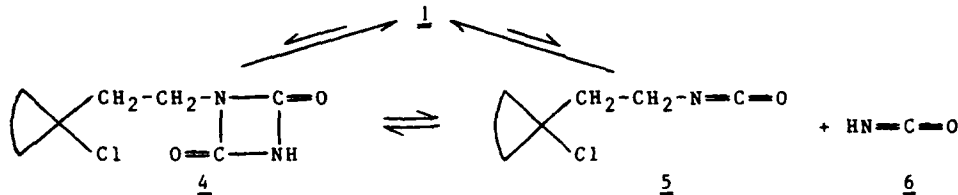
L. Maresca,<sup>a</sup> G. Natile,<sup>a</sup> B. Pelli,<sup>b</sup> and P. Traldi.<sup>b</sup>

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The Pt<sup>IV</sup> complex  $[\text{Pt}(\text{CH}_2\text{CH}_2\text{-NHC=O})\text{Cl}(\text{NCO})(\text{tmen})]$ , 1 (tmen = N,N,N',N'-tetramethylethylenediamine), is generated by reaction of the cationic complex  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}(\text{tmen})]^+$  with cyanate ion which gives nucleophilic attack to the coordinated olefin and oxidative addition to the central metal (the complete reaction requires also the uptake of a proton and of an extra cyanate ion).<sup>1</sup>

Compound 1 exhibits a thermal lability and its rearrangement can be accounted for by the following scheme:



Different combinations of 4, 5, and 6 lead to the formation of 7, 8, and 9 in which one, two or three hydrogens of the 1,3,5-triazine-2,4,6-one eterocycle, CO-NH-CO-NH-CO-NH, have been substituted by R = -CH<sub>2</sub>-CH<sub>2</sub>-Pt(tmen)Cl.

The relative yields of the complexed species (including [Pt(tmen)(NCO)Cl] not reported in the scheme) depends strongly upon the experimental conditions.

M.S. experiments have evidenced the occurrence of a preferred pathway in the decomposition of  $[\text{Pt}(\text{CH}_2\text{CH}_2\text{-NHC=O})\text{Cl}(\text{NCO})(\text{tmen})]$  under E.I., that is elimination of a N-ethylisocyanate fragment either as such or incorporating a second fragment which can be either the coordinated cyanate ion or the tmen ligand.

Both thermal and M.S. experiments indicate that compound 4 is the most likely primary rearrangement product and therefore the process could be described as an intramolecular oxidative addition - reductive elimination reaction.

Work supported by the Ministero Pubblica Istruzione, Roma

<sup>1</sup>L. Maresca and G. Natile, *J. Chem. Soc. Chem. Commun.*, 40 (1983). L. Maresca, G. Natile, A. M. Manotti-Lanfredi, and A. Tiripicchio, *J. Am. Chem. Soc.*, 104, 7661 (1982). G. Gervasio, S. A. Mason, L. Maresca, and G. Natile, *Inorg. Chem.*, 25, 2207 (1986).

CH<sub>2</sub> INSERTION INTO PLATINUM-HALOGEN BONDS

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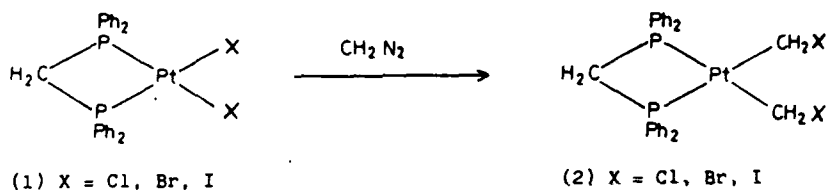
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Nathaniel W. Alcock, Department of Chemistry, University of Warwick, Coventry, U.K.

The insertion of CH<sub>2</sub> into metal-halogen bonds is potentially a convenient route to M-CH<sub>2</sub>X species which are precursors to terminal- or bridging- CH<sub>2</sub> complexes.<sup>1,2</sup>

There has been only one previous report of CH<sub>2</sub> insertion into a transition metal-halogen bond<sup>3</sup> but this reaction is well known in main group chemistry.<sup>4</sup>

We report here the conversion, in high yield, of the dihaloplatinum(II) complexes (1) to the halomethylcomplexes (2):



Complexes (2) have been fully characterized spectroscopically and the X-ray crystal structure of (2, X=Cl) has been determined.

The scope of this reaction and some of the chemistry of the reactive complexes (2) will be discussed.

This project has been supported by a NATO travel grant.

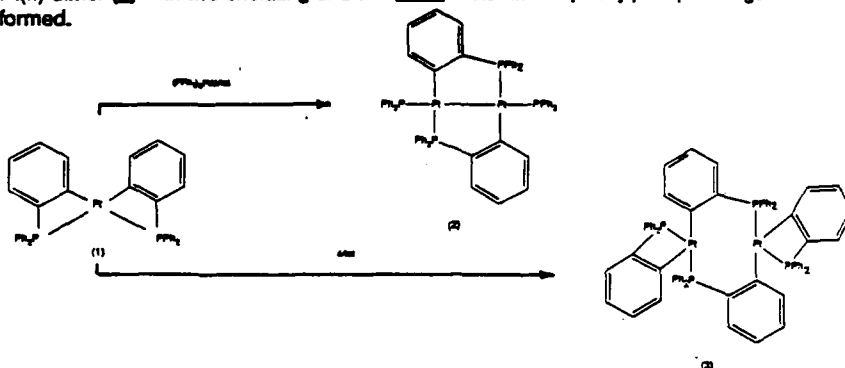
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# **Synthesis and Properties of Dinuclear Complexes of Platinum(I) and Platinum(II) Containing Bridging *Ortho*-metallated Triphenylphosphine Ligands**

Johannes Messelhäuser, Martin A. Bennett, Suresh K. Bhargava, Evert J. Ditzel, Glen B. Robertson, Anthony C. Willis, David E. Berry

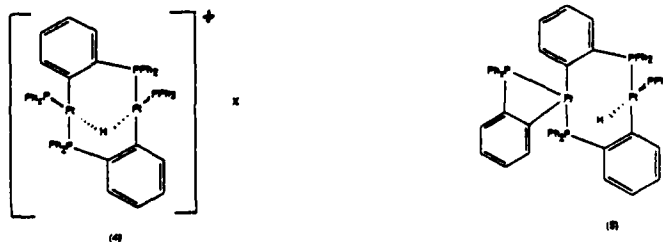
Australian National University, Research School of Chemistry, G.P.O. Box 4, CANBERRA, ACT 2601

The comproportionation of the bis(chelate)complex  $[(o-C_6H_4)PPh_2]_2Pt$  (1) and  $(PPh_3)_3Pt$  in hot toluene gives the dinuclear Pt(I)-complex (2) containing a Pt-Pt bond, two terminal and two bridging *ortho*-metallated  $PPh_3$  ligands.<sup>1)</sup> On heating (1) in the absence of  $(PPh_3)_3Pt$  the Pt(II) dimer (3) with two chelating and two *ortho*-metallated triphenylphosphine ligands is formed.



In (1) the terminal  $PPh_3$  ligand can easily substituted by  $tBuNC$  affording  $(tBuNC)_2(\mu-o-C_6H_4PPh_2)_2Pt$ .

The Pt-Pt bond of (2) is cleaved by various acids  $HX$  ( $X = BF_4, CF_3COO, CF_3SO_3, toSO_3$ ) forming a Pt-H-Pt bridge (4). Bases as  $K_2CO_3$  or  $NH_3$  replace the proton of the Pt-hydride complex (4) leading to the original complex (2). With  $BuLi$ , however, an isomer of (2) is formed, which is tentatively assigned structure (5).



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## NEUTRAL PERHALOPHENYL BINUCLEAR PLATINUM-SILVER COMPLEXES

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We have recently prepared polynuclear perhalophenyl complexes containing Pt  $\rightarrow$  Ag bonds, by reacting anionic perhalophenyl platinate(II) derivatives with  $\text{ClO}_4\text{Ag}$  or  $\text{O}_3\text{ClOAgL}$  (1). The structure of the obtained complexes is strongly dependent on the nature of the platinum precursors and in most of these complexes the perhalophenyl groups are oriented in such a way that one of the o-F or o-Cl atoms of the perhalophenyl groups makes a short contact with the silver atom.

$(\text{NBu}_4)|\text{Pt}(\text{C}_6\text{F}_5)_3\text{L}|$  ( $\text{L} = \text{N}, \text{P}, \text{S}$  donor) react with  $\text{O}_3\text{ClOAgL}'$  ( $\text{L}' = \text{PPh}_3, \text{PEt}_3$ ) yielding the binuclear  $|\text{L}(\text{C}_6\text{F}_5)_3\text{Pt} \rightarrow \text{AgL}'|$  derivatives (2) and in order to evaluate the influence of the ligands bonded to the platinum centre we have prepared the following complexes:  $(\text{NBu}_4)|\text{cis-Pt}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Cl}_5)\text{L}|$ ,  $(\text{NBu}_4)|\text{cis-Pt}(\text{C}_6\text{F}_5)(\text{C}_6\text{Cl}_5)_2\text{L}|$ ,  $(\text{NBu}_4)|\text{trans-PtX}_2(\text{C}_6\text{F}_5)\text{L}|$ ,  $(\text{NBu}_4)|\text{trans-PtX}_2(\text{C}_6\text{Cl}_5)\text{L}|$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and have studied their reactions with  $\text{O}_3\text{ClOAgPPh}_3$ . In all cases binuclear platinum silver derivatives of general formula  $|\text{L}(\text{C}_6\text{F}_5)_x(\text{C}_6\text{Cl}_5)_y\text{PtAgPPh}_3|$  ( $x = 1, y = 2; x = 2, y = 1$ ) or  $|\text{L}(\text{C}_6\text{X}'_5)\text{X}_2\text{PtAgPPh}_3|$  ( $\text{X} = \text{Cl}, \text{Br}, \text{X}' = \text{Cl}, \text{F}$ ) have been obtained. Crystallographic studies reveal that o-Cl...Ag contacts are stronger than the o-F...Ag ones since the higher electronegativity of the fluorine makes it more reluctant to donate electron density to the silver centres.

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PREPARATION AND STRUCTURAL CHARACTERIZATION OF  $\text{BIS}(1,5\text{-CYCLOOCTADIENE})\text{-COPPER(I) PERCHLORATE}$  AND THE NATURE OF  $\text{Cu-OLEFIN}$  BONDING.

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The binary copper(I) complex with a olefin,  $[\text{Cu}(\text{cod})_2]\text{ClO}_4$  (cod = 1,5-cyclooctadiene), was synthesized by the reduction of copper(II) perchlorate with copper wire in the presence of cod. The structure has been determined by a single-crystal X-ray structure analysis and the nature of Cu-olefin bonding has been discussed on the basis the C=C distance,  $^1\text{H}$  NMR chemical shifts and  $\nu(\text{C}=\text{C})$ . Three important results emerge from this study. Firstly, the obtained molecular structure is the first binary Cu(I) complex with olefin of which geometry is characteristic of a four-coordinate tetrahedron regarding four olefin bond moieties of two cod molecules (Figure 1). Secondly, the Cu-olefinic carbon distances  $\{\text{Cu}-\text{C} = 2.273 \text{ \AA}(\text{av.})\}$  are significantly longer than those  $(1.93 - 2.07 \text{ \AA})$  for the mixed-ligand Cu(I) olefin complexes reported,<sup>1</sup> suggesting that the metal-olefin bonding mode in four-coordinate copper(I) complexes is almost purely dominated by  $\sigma$  donation. On the other hand, some mixed-ligand Cu(I) complexes with both olefins and nitrogenous ligands show a slight increase in the contribution of  $\pi$  back donation in the bonding mode, because the shortening of the Cu-olefin bond due to replacement of one olefin with a nitrogenous ligand implies the strengthening of  $\pi$  back bonding. This is also supported from the fact that the  $^1\text{H}$  NMR spectrum of olefinic protons of the cod molecule appeared lower field compared with that for free cod.<sup>2</sup> Thirdly, the coordination of the cod molecules to the Cu(I) ion exerts virtually no effect on the C=C bond distances of the coordinated cod molecules:  $1.332 \text{ \AA}(\text{av.})$  vs  $1.341 \text{ \AA}(\text{av.})$  for free cod molecule. This phenomenon is also reflected on the little decreasing of the C=C stretching frequencies,  $69 \text{ cm}^{-1}$ .

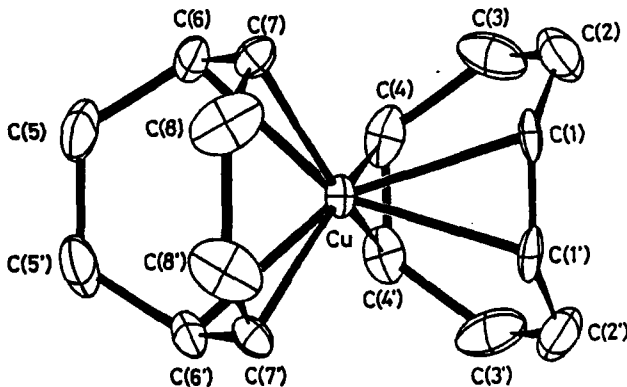


Figure 1. Structure of  $[\text{Cu}(\text{cod})_2]^+$

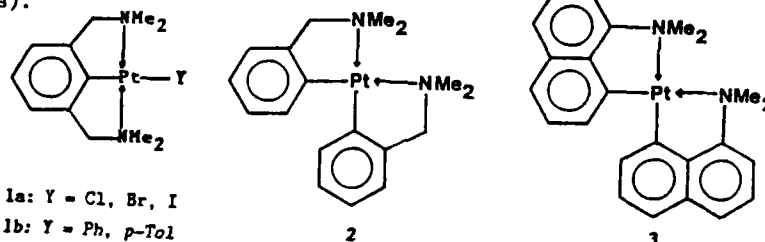
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**Stereoselective Oxidative Addition Reactions of Halogens and Copper(II) Halides to Square Planar Organoplatinum(II) Complexes.**

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Oxidative addition reactions of electrophiles to organometallic complexes play an important role in both organometallic synthesis and in many homogeneous catalyzed processes. We studied the reactions of halogens and copper(II) halides with the organoplatinum(II) complexes 1, 2 and 3 (see figures).



Reactions with  $\text{CuX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) yielded for 2 and 3  $\text{cis-X}_2\text{Pt(IV)}$  products (for 1a  $\text{mer-X}_3$  arrangement), whereas the reactions of 2 and 3 with the halogens  $\text{Br}_2$  and  $\text{I}_2$  yielded  $\text{trans-X}_2\text{Pt(IV)}$  oxidative addition products. For steric reasons implied by the rigid terdentate ligand system, 1b reacted with  $\text{X}_2$  to afford  $\text{cis-X}_2\text{Pt(IV)}$  complexes. Most strikingly, 1a (with  $\text{Y} = \text{I}$ ) reacted with  $\text{I}_2$  to yield the first example of a complex with an  $\text{I}_2$  molecule  $\eta^1$  bonded to the  $\text{Pt(II)}$  centre,<sup>1</sup> a situation that can be seen as an early stage in the oxidative addition reactions of halogens to  $\text{Pt(II)}$ . The above described results (isolation of the  $\text{I}_2$ -intermediate and the stereochemistry of the  $\text{Pt(IV)}$  products), obtained by suitable choice of the chelate ligands, indicate that the oxidative addition reactions of halogens to square planar organoplatinum(II) complexes most probably proceed via the  $\text{S}_{\text{N}}2$  type mechanism.

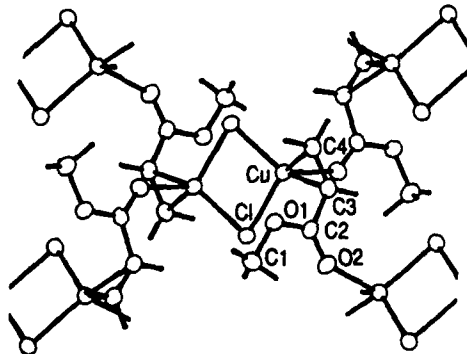
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PREPARATION AND STRUCTURES OF COMPLEXES BETWEEN  $\alpha,\beta$ -  
UNSATURATED CARBONYL COMPOUNDS AND COPPER(I) CHLORIDE

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$\pi$ -Complexes between  $\alpha,\beta$ -unsaturated carbonyl compounds and copper(I) are of interest in relation to the tendency of copper(I) to promote conjugate addition reactions. We have previously reported the preparation and structural characterisation of complexes between copper(I) chloride and acrylaldehyde [1], methyl vinyl ketone [2] and ethyl vinyl ketone [3]. In the first compound, the acrylaldehyde ligand has the *s-trans* conformation, and acts as a bridge, via C=C and the carbonyl oxygen atom, between adjacent Cu(I). In the second, there are two types of butenone ligand: one bridging, with the *s-trans* conformation and one terminal, *s-cis*, bonded to Cu(I) solely via C=C. The pentenone ligand in the third compound is an *s-cis* bridge with a long O-Cu bond. In the complex between methyl acrylate and copper(I) chloride, the ligand assumes the *s-trans* conformation, rather than the preferred [4] *s-cis* conformation of the uncomplexed molecule, bridging (CuCl)<sub>2</sub> dimers to form layers:

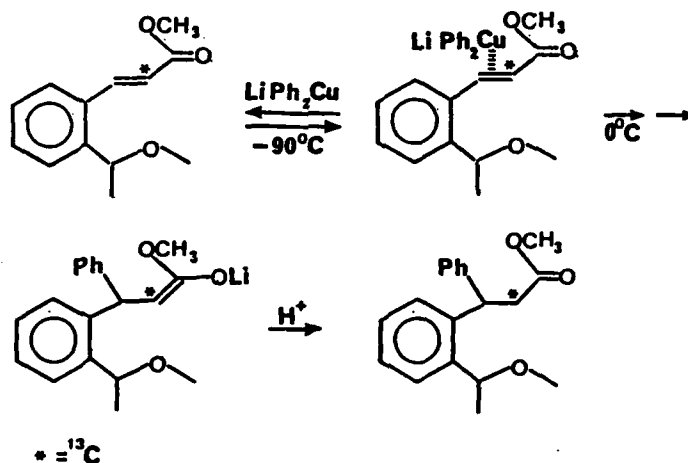


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ORGANOCUPRATE ADDITION TO  $\alpha,\beta$ -UNSATURATED COMPOUNDS:  
NMR INVESTIGATIONS

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The addition of lithium dimethylcuprate and lithium diphenylcuprate to methyl 2-(1-methoxyethyl)cinnamate has been investigated by NMR spectroscopy. The experiments were run at various temperatures,  $-90$  -  $+20^\circ\text{C}$ , in order to study the formation and dynamics of an copper-alkene  $\pi$ -complex. The substrate was labeled with  $^{13}\text{C}$  in the  $\alpha$ -carbon position to facilitate the assignments.



The signals at 50 - 54 ppm ( $-90^\circ\text{C}$ ) have been assigned to the  $\alpha$ -carbon of isomeric copper-alkene  $\pi$ -complexes. As the temperature was increased these signals disappear with the simultaneous increase of signals assigned to the product enolate.

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## SYNTHESIS AND STRUCTURAL STUDIES ON

## COPPER (I) COMPOUNDS

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We have been developing a programme on metal carbonyl chemistry (1, 2) for some years and now we wish to report our findings concerning to the study of bimetallics that have Cu-Fe bonds. These complexes of general formula  $[LCu_2Fe(CO)_4]$  (L = ethylenediamine, N,N'-dimethylethylenediamine; N,N'-diethylethylenediamine; N,N,N',N'-tetramethylethylenediamine; diethylenetriamine) were synthesized in water by reacting  $[Fe(CO)_5]$  and CuCl in the presence of the nitrogen ligands. They are yellow solids and their infrared spectra in the  $\nu CO$  region suggest that the symmetry around the iron is octahedral with the Cu atoms at cis-positions. As some CO modes are observed in the range  $1800-1700\text{ cm}^{-1}$  it is possible that these compounds have CO bridging groups.

We are also interested in copper(I)-triphenylphosphine complexes (3) and recently we run the reaction of the dimer  $[CuSCN(PPh_3)_2]$  with  $\theta$ -phenanthroline. The structure of the product  $[CuSCN(phen)(PPh_3)]$ , was determined by X-ray diffraction and consists of a monomer with the copper atom tetrahedrally coordinated. Some important distances and bond angles are:

Cu-P = 2,2091(4) Å	$N_2\text{-Cu-N}_3 = 103,5(6)^\circ$
Cu-N <sub>2</sub> = 2,02(2) Å	$N_2\text{-Cu-N}_4 = 111,3(5)^\circ$
Cu-N <sub>3</sub> = 2,31(1) Å	$N_3\text{-Cu-P} = 120,6(4)^\circ$
$N_2$ (nitrogen of SCN)	
$N_3$ and $N_4$ (nitrogen of phen)	

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PREPARATION AND CHARACTERISATION OF SOME Cu(II), Ni(II)  
AND Co(II) SCHIFF BASE CHELATES OF QUINOLINE TYPE

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In continuation of the other studies on the preparation and investigation of some Schiff's bases as the ligands in the metal chelates, the following azomethine compounds of quinolyne type were synthesized:

1,6-di-(2-quinolyl)-2,5-diazo-1,5-hexadiene and

4-(2-quinolylmethylene-amino-1-phenyl-2,3-dimethyl-5-pyrazolone.

The structure of these azomethine compounds were confirmed by means of elemental analyses, UV/VIS, IR and MS analytical methods. Their Cu(II) and Ni(II) metal complexes were prepared in general with Cu(II)-chloride, Ni(II)-acetate, precipitated and isolated as perchlorates. The nature of bonding by forming complex molecules was determined via UV/VIS, IR as well as by mass spectra.

## NEW YLIDE-COMPLEXES OF Ag, Au, Pd, AND Pt.

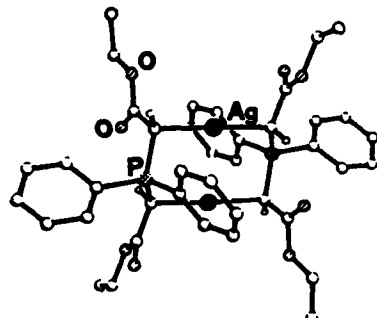
Jose Vicente, Maria-Teresa Chicote, Isabel Saura-Llamas and Juan Fernandez-Baeza. Departamento de Quimica Inorganica, Universidad de Murcia, 30.071 Murcia, Spain.

Peter G. Jones, Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, W. Germany.

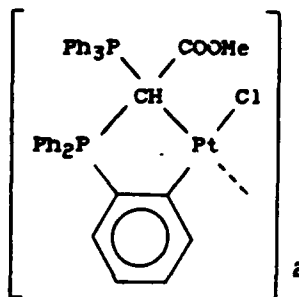
The phosphonium salt  $[\text{Ph}_2\text{P}(\text{CH}_2\text{COOEt})_2]\text{Cl}$  reacts with  $\text{Ag}_2\text{CO}_3$  (1:1) to give the dinuclear complex  $[\text{Ag}_2\{\mu-[(\text{CH}(\text{COOEt}))_2\text{PPh}_2]\}_2]$  (1) which crystal structure has been determined. (1) reacts with  $[\text{AuCl}(\text{tht})]$  (tht = tetrahydrothiophene) (1:2) to give the analogous Au(I) complex that can be oxidized with  $\text{Cl}_2/\text{Ph}$  or  $\text{I}_2$  to the corresponding Au(II) derivatives even if an excess of the oxidizing agent is used.

When  $[\text{Ph}_2\text{P}(\text{CH}_2\text{COOEt})_2]\text{ClO}_4$  is reacted with  $[\text{Au}(\text{acac})\text{L}]$  [L:  $\text{PPh}_3$ ,  $\text{P}(3\text{-CH}_3\text{O-C}_6\text{H}_4)_3$ ] trinuclear cationic complexes are obtained as a result of the substitution of three hydrogen atoms of the phosphonium salt by three "AuL" moieties.

On the other hand,  $\text{PtCl}_2$  reacts with  $\text{Ph}_3\text{PCHCOOCH}_3$  to give a dinuclear complex (2) where the ylide is orthometallated.



$[\text{Ag}_2\{\mu-[(\text{CH}(\text{COOEt}))_2\text{PPh}_2]\}_2]$  (1)



(2)

When (2) is reacted with 1,10-phenanthroline in the presence of  $\text{NaClO}_4$ , a cationic complex is obtained. Both species can be oxidized with  $\text{Cl}_2/\text{CCl}_4$  to the corresponding neutral or cationic Pt(IV) complexes.

If  $[\text{PtCl}_2(\text{NCC}_6\text{F}_5)_2]$  is reacted with different ylides of general formula  $\text{Ph}_3\text{PCHCOR}$ , complexes of the types  $[\text{PtCl}_2\{\text{N}=\text{C}[\text{CH}(\text{PPh}_3)\text{COR}](\text{C}_6\text{F}_5)_2\}]$  (R: OMe, OEt) or  $[\text{PtCl}_2\{\text{NH}[\text{C}=\text{C}(\text{PPh}_3)\text{COR}](\text{C}_6\text{F}_5)_2\}]$  (R: Me, Ph) are obtained.

**SILVER FERROCENE-LIGAND COMPLEXES: DONOR PREFERENCE AND REDOX PROPERTIES**

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William R. Cullen, Department of Chemistry, University of British Columbia, Vancouver, Canada.

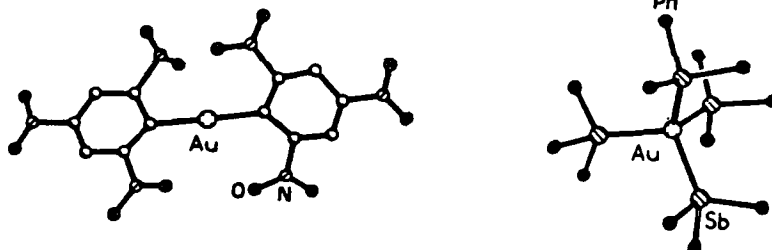
Silver(I) complexes of the chelating ferrocene ligands  $\text{Fe}[\text{C}_5\text{H}_4(\text{PR}_2)]_2$ ,  $\text{CpFe}[\text{C}_5\text{H}_3(\text{CH}(\text{R})\text{NMe}_2)(\text{PR}_2)]$  and  $[\text{C}_5\text{H}_4(\text{PR}_2)]\text{Fe}[\text{C}_5\text{H}_3\text{CH}(\text{R})\text{NMe}_2](\text{PR}_2)]$  have been synthesised and the donor preference and structure investigated by  $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{109}\text{Ag}$  NMR and X-ray crystal data. In all cases the overall stoichiometry is  $[\text{AgL}_2]^+\text{X}^-$  in the solid but in solution all complexes are stereochemically non-rigid with tri-substituted complexes as well as species involving -N, -N/P or P/P donor sets, being observed. Cyclic voltammetry and chemical studies show that both the ferrocene and silver redox centres can be oxidised giving the first Ag(II)-phosphine complexes; the interaction between these two redox centres will be discussed. Where there is a -N/P donor set the silver(I) complexes undergo a novel cleavage of the  $\text{NMe}_2$  group.

## 2,4,6-TRINITROPHENYL COMPLEXES OF Au(I) AND Pd(II)

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There exists just one 2,4,6-trinitrophenyl complex of a transition element [1]. We have succeeded in preparing Au and Pd derivatives using the corresponding diarylmercury(II) compound. Thus, by reacting  $[\text{AuCl}_2]^-$  with  $\text{HgR}_2$  ( $\text{R} = 2,4,6$ -trinitrophenyl) (1/1) we prepared  $[\text{Au}(\text{R})\text{Cl}]^-$  (1) which reacts with  $\text{NaClO}_4$  + tetrahydrothiophene(tht) to give  $[\text{Au}(\text{R})(\text{tht})]$  (2) which its high stability must be assigned to the special nature of the R group. Complex 2 reacts with ligands  $\text{L}_2$  to give complexes " $\text{Au}(\text{R})\text{L}_2$ " [ $\text{L} = \text{SbPh}_3$  (3) or  $\text{L}_2 = 1,10$ -phenanthroline (4)]. The crystal structure of complex 3 corresponds to a formulation  $[\text{Au}(\text{R})_2][\text{AuL}_4]$ .



Treatment of  $[(\text{PhCH}_2)\text{PPh}_3]_2[\text{Pd}_2\text{Cl}_4(\mu\text{-Cl})_2]$  with  $\text{HgR}_2$  (1/2) in refluxing acetone gives  $[(\text{PhCH}_2)\text{PPh}_3]_2[\text{Pd}_2\text{R}_2\text{Cl}_2(\mu\text{-Cl})_2] \cdot 2\text{Me}_2\text{CO}$  (5). The reaction of 5 with excess of  $\text{NaX}$  gives  $[(\text{PhCH}_2)\text{PPh}_3]_2[\text{Pd}_2\text{R}_2\text{X}_2(\mu\text{-X})_2]$  [ $\text{X} = \text{Br}$  (6),  $\text{I}$  (7)]. Reactions of 5 or 6 with dimethylsulfoxide lead to complexes  $\text{cis-}[(\text{PhCH}_2)\text{PPh}_3][\text{Pd}(\text{R})\text{X}_2(\text{S}(\text{O})\text{Me}_2)]$  [ $\text{X} = \text{Cl}$  (8),  $\text{Br}$  (9)]. Complex 5 reacts with several mono- and bi-dentate ligands to give neutral complexes  $[\text{Pd}(\text{R})\text{ClL}_2]$ . Some of these react with  $\text{AgClO}_4$  to give stable perchlorato-complexes  $[\text{Pd}(\text{R})(\text{OClO}_3)_2\text{L}_2]$  which in turn react with bidentate neutral ligands  $\text{L}'_2$  to give complexes  $[\text{Pd}(\text{R})\text{L}'_2\text{L}]^+$  or with  $\text{PPh}_3$  to give complexes  $[\text{Pd}(\text{R})\text{L}_2(\text{PPh}_3)]^+$ .

[1] W. Beck, K. Schorpp, and K. H. Setter, Z. Naturforsch B., 26(1971)684

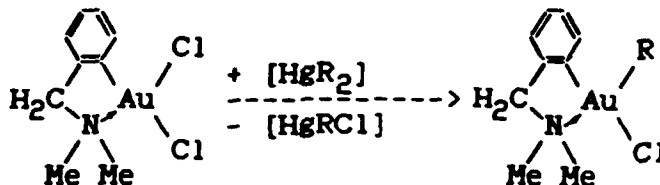
## THE ORGANOMERCURY ROUTE TO MIXED DIARYLGOLD(III) COMPLEXES

-Jose Vicente, Maria-Teresa Chicote, Maria-Dolores Bermudez, Maria-Jose Sanchez-Santano. Departamento de Química Inorganica, Universidad de Murcia, 30.071 Murcia, Spain.

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We have used organomercury compounds as transmetallating reagents in the synthesis of arylgold(I) and (III) complexes [1]. The complexes obtained in these transmetallation reactions are mono- or di-aryl complexes depending on the nature of the aryl group to be transferred, on the oxydation state of gold and on the reaction conditions.

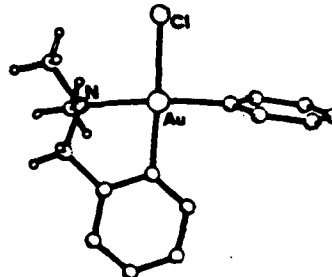
By reacting monoarylgold(III) complexes with organomercurials, mixed diaryl derivatives can be isolated. We illustrate this synthetic method through the following general reaction:



R = 2-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NHMe<sub>2</sub>, 2-C<sub>6</sub>H<sub>4</sub>N=NPh, Ph, C<sub>6</sub>F<sub>5</sub>, 2-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, 2- or 3-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>.

We also report the synthesis of derivatives of these mixed diaryl complexes obtained by reacting them with neutral and anionic ligands.

We also present the first crystal structure of a neutral mixed diarylgold(III) complex which confirms many structural and IR spectral assignments that we have previously done.



---- Crystal Structure of  
[Au(2-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NHMe<sub>2</sub>)(Ph)Cl]

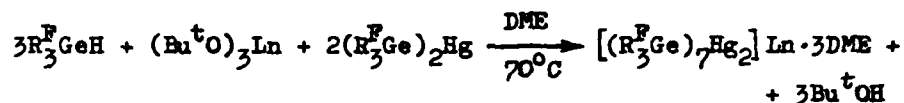
[1] J. Vicente, M.T. Chicote, M.D. Bermudez, M.J. Sanchez-Santano, P.G. Jones, C. Pittschen and G.M. Sheldrick, J. Organomet. Chem. 310 (1986) 401 and refs. there in.

GERMYLMERCURY COMPLEXES OF TRIVALENT SAMARIUM, EUROPIUM AND YT-  
TERBIUM

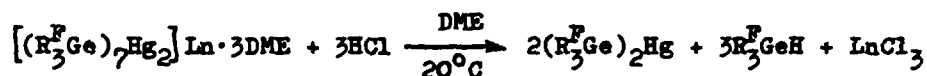
N.A.Orlov, S.F.Zhiltsov, L.N.Bochkarev, Gorky state pedagogical  
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Earlier we have found [1], that interaction of metallic samarium, europium and ytterbium with germylmercury  $[(C_6F_5)_3Ge]_2Hg$  in 1,2-dimethoxyethane (DME) leads to the formation of ionic germylmercury complexes of divalent lanthanoids  $[(R_3^FGe)_6Hg_2]^{2-} Ln^{2+}$  ( $R^F = C_6F_5$ ).

In this paper we report that similar germylmercury complexes of trivalent samarium, europium and ytterbium have been obtained by hydride method - reaction of hydride  $R_3^FGeH$  with tert-butoxyderivatives of lanthanoids in the presence of  $(R_3^FGe)_2Hg$



The isolated compounds of samarium, europium and ytterbium react easily with hydrogen chloride and at molar reagent ratio 1:3 give germylmercury hydride  $R_3^FGeH$  and  $LnCl_3$  in high yields:



Furthermore, it was found that the reaction of  $(R_3^FGe)_2Hg$  with  $YbI_3$  in DME or methyl cyanide leads to the formation of germylmercury complex of trivalent ytterbium  $[(R_3^FGe)_2HgI]_3^{1-} Yb^{3+}$ .

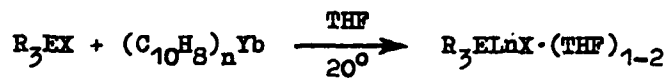
1. L.N.Bochkarev, N.A.Orlov, S.F.Zhiltsov, M.N.Bochkarev. Zh. Obshch.Khimii, 52, (1987), 2804.

ORGANOSILICON, -GERMANIUM AND -TIN COMPLEXES OF LANTHANOIDS OF  
GRIGNARD REAGENTS TYPE

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Earlier we have found that reaction of organogermanium and -tin halogenides  $R_3EX$  ( $E = Ge, Sn; X = Br, I$ ) with metallic samarium, europium and ytterbium in THF solution leads to the formation of complexes  $R_3ELnX \cdot (THF)_{1-2}$  in low yields. Chlorides  $R_3ECl$  ( $E = Si, Ge, Sn$ ) in similar conditions do not react with metallic lanthanoids.

Now we report that Grignard type complexes  $R_3ELnX$  can be obtained in more high yields by reaction of organosilicon, -germanium and -tin iodides, bromides and also chlorides with naphtalene derivatives of lanthanoids



$Ln = Sm, Eu, Yb; E = Si, Ge, Sn; X = Cl, Br, I; R = Me, Et, Ph;$   
 $n = 0,5-1$

Complexes  $Et_3GeYbBr \cdot (THF)_2$ ,  $Ph_3SnYbCl \cdot (THF)_2$ ,  $Me_3SiYbCl \cdot (THF)_2$  have been isolated in 74%, 30%, 25% accordingly. The compounds are deep-brown solid substances, unstable in air, well soluble in THF, 1,2-dimethoxyethane, insoluble in hexane.

Organogermanium and -tin complexes of lanthanoids react with  $Et_3GeBr$  and  $Ph_3SnCl$  with the formation of halogenides of divalent lanthanoids  $LnX_2$  and  $Et_6Ge_2$  or  $Ph_6Sn_2$  accordingly.

Reaction of  $Me_3SiYbCl$  with trimethylchlorosilane leads to oxidation of ytterbium to trivalent state:



Reaction of  $Me_3SiYbCl_2$  derivative with  $Me_3SiCl$  leads to  $YbCl_3$  and  $Me_6Si_2$ .



MONOCYCLOPENTADIENYL LANTHANIDE(III) COMPLEXES. II. CONFORMATIONAL CHANGES IN THE SOLID STATE STRUCTURE OF SAMARIUM(III) AND EUROPIUM(III) ORGANOMETALLIC DERIVATIVES.

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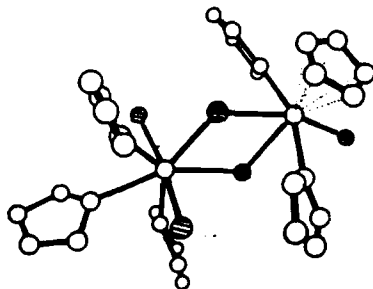
In the preceding Abstract (Part I) the structure of the europium (III) complex  $(\eta^5\text{C}_5\text{H}_5)\text{EuCl}_2(\text{THF})_3$  is described. The X-ray structural results show that the compound assumes a distorted mer,trans octahedral configuration as in the erbium(III) analogous. (1)

We have extended our investigation to samarium(III) and gadolinium(III) monocyclopentadienyl complexes in order to check if the observed tendency to give the above geometry is general. We report here the crystallographic results on the samarium(III) compound obtained by reacting  $\text{SmCl}_3$  with  $\text{NaC}_5\text{H}_5$  in tetrahydrofuran (molar ratio=1).

**Crystal data.** Yellow pale crystals of  $(\eta^5\text{C}_5\text{H}_5)\text{Sm}_2\text{Cl}_5(\text{THF})_5$  are monoclinic, space group  $\text{P2}_1/\text{c}$ , with  $a=16.615(3)$ ,  $b=17.766(3)$ ,  $c=13.440(2)$  Å,  $\beta=104.0(2)^\circ$ ,  $Z=4$ ,  $V=3849.4$  Å<sup>3</sup>.

The samarium(III) compound has different stoichiometry and overall geometry as compared with that of the  $\text{EuCl}_3\text{-NaC}_5\text{H}_5$

reaction under apparently similar conditions. The molecular structure of the samarium compound consists of dinuclear units in which the samarium atoms are bridged by two chlorine atoms and have different environment. The distances are: Sm-Sm, 4.443 Å; Sm-Cl(bridge) av., 2.80 Å. This distance is 0.2 Å longer than that to the other chlorine atoms. The Cl-Sm-Cl angles of the bridging unit are  $75^\circ$ . One



samarium atom is heptacoordinated being surrounded by four chlorine atoms and three THF molecules, the other is hexacoordinated by three chlorine atoms, two THF ligands and a cyclopentadienyl ring bonded in a penta-hapto fashion.

REFERENCE.

- 1) C.S. Day, V.W. Day, R.D. Ernst and S.H. Vollmer, *Organometallics*, 1, 998, (1982).

## IODIZED MISCH METAL AS A SYNTHETIC AGENT

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Misch metal, an alloy of lanthanoid metals, easily reacts with 1,2-diiodoethane in THF. The resulting iodized misch metal solution was tested about its reactivity toward a variety of functional groups.

Epoxides were deoxygenated. Aldehydes and ketones were reduced in the presence of alcohol to primary and secondary alcohols. Acyl and benzyl halides gave only coupling products. Bis(halo-methyl)benzenes gave [2.2]cyclophanes as coupling products. In the absence of alcohol, aldehydes and ketones gave pinacols. Treatment of a mixture of aldehyde or ketone and alkyl or benzyl halide with the iodized misch metal gave a mixture of products: pinacol, Grignard adduct, reduction product and/or diphenylethane. A similar treatment of aldehydes or ketones and  $\alpha$ -halogeno-alkanoates gave Reformatsky adducts in high yields.

In a similar way, cerium reacted easily with 1,2-diiodoethane in THF and the product showed a similar reactivity to the iodized misch metal.

It can thus be concluded that both iodides are synthetic agents comparable to  $\text{SmI}_2$ .

SYNTHESIS AND CHARACTERIZATION OF SOME DIVALENT  
LANTHANIDE ORGANOMETALLIC COMPLEXES

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Tennessee 37831 USA

In an attempt to synthesize divalent complexes of californium and possibly americium, some preliminary studies involving europium, ytterbium, and samarium have been carried out using cyclopentadienyl, indenyl, pentamethylcyclopentadienyl, and pentaphenylcyclopentadienyl ligands. Because of the innate problems associated with both californium and americium (high specific activity and quantities available), the more completely we can characterize the lanthanide complexes, and also perfect techniques for small scale syntheses, the easier the actinide studies should be. Because the (II/III) potentials of samarium and californium are similar (approximately 1.7V vs the normal hydrogen electrode) if we can prepare the bis samarium complex we should be able to prepare the corresponding californium complex. Americium on the other hand has a (II/III) potential of approximately 2.6V vs the NHE, so this will present more problems. The lanthanide work and also possible synthetic routes for the actinide work will be discussed here.

Ortho-substitution of Aromatic Substrates Using Electrophiles  
and Palladium Acetate

Samuel J. Tremont\*, Lanny Liebeskind, John Gasdaska,  
Barry L. Haymore and Dominic McGrath

Abstract:

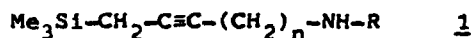
Ortho-alkyl acetanilides have been prepared in high yields under mild conditions by the reaction of acetanilides,  $\text{Pd}(\text{OAc})_2$  and alkyl halides. This new synthetic method can be used to synthesize a variety of highly functionalized mono- or di-ortho-alkyl acetanilides. The ortho alkylation reaction can be made catalytic in palladium by using excess  $\text{AgOAc}$ . The reaction involves the initial formation of an ortho-palladated acetanilide complex; this complex is then alkylated with alkyl halide by a non radical pathway. This new ortho-substitution reaction has also been demonstrated with many non-carbon electrophiles to produce a family of ortho-substituted products. Application of this chemistry to other aromatic substrates has also been studied.

REACTIONS OF IN SITU GENERATED IMINIUM IONS  
WITH PROPARGYLSILANES

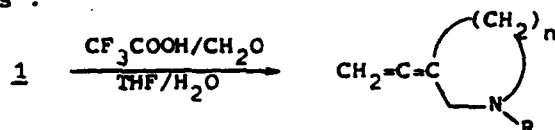
Jacques PORNET , Dominique DAMOUR and Léone MIGINIAC ,  
Laboratoire de Synthèse Organique, UA CNRS 574, Université de  
Poitiers, 40, avenue du Recteur Pineau, 86022 Poitiers, France

We have shown that  $\omega$ -silyloxypropargyltrimethylsilanes are convenient precursors for the preparation of 3-vinylidene oxygen-containing heterocycles (1,2).

We report a new method to prepare 3-vinylidene nitrogen-containing heterocycles (3), from  $\omega$ -monoalkylaminopropargyltrimethylsilanes 1 :



Upon exposure to silanes 1 , simple iminium ions generated in situ under Mannich-like conditions from formaldehyde, afford in a one-pot reaction 3-vinylidene pyrrolidines, piperidines and perhydroazepines :



Scope and limitations of this reaction will be discussed.

- (1) J. PORNET, D. DAMOUR and L. MIGINIAC, Tetrahedron, 1986, 42, 2017.
- (2) J. PORNET, D. DAMOUR, B. RANDRIANOELINA and L. MIGINIAC, Tetrahedron, 1986, 42, 2501.
- (3) D. DAMOUR, J. PORNET and L. MIGINIAC, Tetrahedron Lett., 1987, 28, 4689.

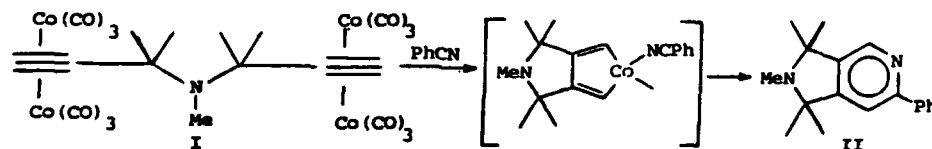
## PYRIDINES FROM NITRILE-DIALKYNE COCYCLIZATION ON Co(0) AND Co(I) COMPLEX

Luigi Pietro Battaglia, Daniele Delledonne, Mario Nardelli, Giovanni Predieri, Istituto di Chimica Generale ed Inorganica dell'Universita', Viale delle Scienze, I-43100 Parma, Italy

Gian Paolo Chiusoli, Mirco Costa, Istituto di Chimica Organica, Universita', Viale delle Scienze, I-43100 Parma, Italy

Corrado Pelizzi, Istituto di Chimica Biologica, Via Murani 23/a, I-07100 Sassari

Dicobalt octacarbonyl and N-methyldi( $\alpha,\alpha$ -dimethylpropargyl)amine give complex I, the structure of which has been determined by X-ray methods. We examined its reactivity with benzonitrile and the reactivity of the amine with benzonitrile and dicobalt octacarbonyl in comparison with other Co(0) and Co(I) complexes. We observe that dicobalt octacarbonyl reacts with a selectivity comparable to that of bis(acetonitrile)bis(diethyl fumarate)cobalt(0) to give II. This means that complex I must undergo rearrangement and fragmentation to give the expected cobaltacycle precursor of II.



The ability of Co(0) to incorporate nitriles is essentially due to the presence of the geminal groups on the substrate. In the absence of such groups the reaction of nitriles become difficult and the acetylenic triple bond is incorporated preferentially. Thus 1,7-octadiyne and 1,6 heptadiyne have been caused to react with monomeric, dimeric and heterogeneous cobalt(0) catalysts, i.e. (bis(acetonitrile)bis(diethyl fumarate)cobalt) (dicobalt octacarbonyl) and  $\text{CoCl}_2/\text{Mn}$  in comparison with cyclopentadienylbis(triphenylphosphine)cobalt(I). The latter turns out to be the best catalyst for nitrile incorporation. The other catalysts prefer the acetylenic triple bond. The heterogeneous cobalt catalyst is the most selective for the acetylenic triple bond but also is the most sensitive to the action of geminal groups, which cause a reactivity change leading to preferential nitrile incorporation.

The reactivity change seems to be determined by the combination of steric and conformational effects: the latter favor the cobaltacycle ring formation the former makes more difficult the incorporation of an acetylenic molecule into the cobaltacycle, thus favoring the nitrile incorporation.

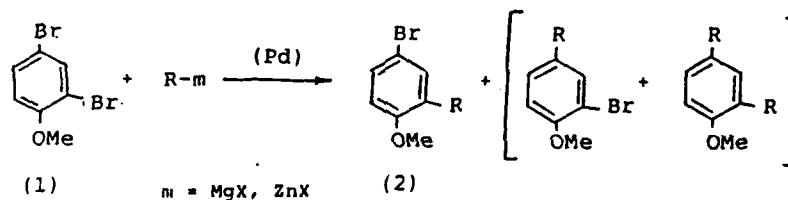
Work supported by Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione.

## REGIO-SELECTIVE MONO-ALKYLATION OF 2,4-DIBROMOANISOLE

## CATALYSED BY PALLADIUM-PHOSPHINE COMPLEXES

Akio Minato, Yasuhiro Fujiwara, Sigeru Ozasa, Kyoto  
Pharmaceutical University, Misasagi, Yamashina, Kyoto 607,  
JAPAN

The regio-selective introduction of organic groups into an aromatic ring has been a fundamental subject of synthetic organic chemistry. We report here the palladium-phosphine complex-catalysed regio-selective mono-alkylation of 2,4-dibromoanisole (1) by Grignard and organozinc reagents.



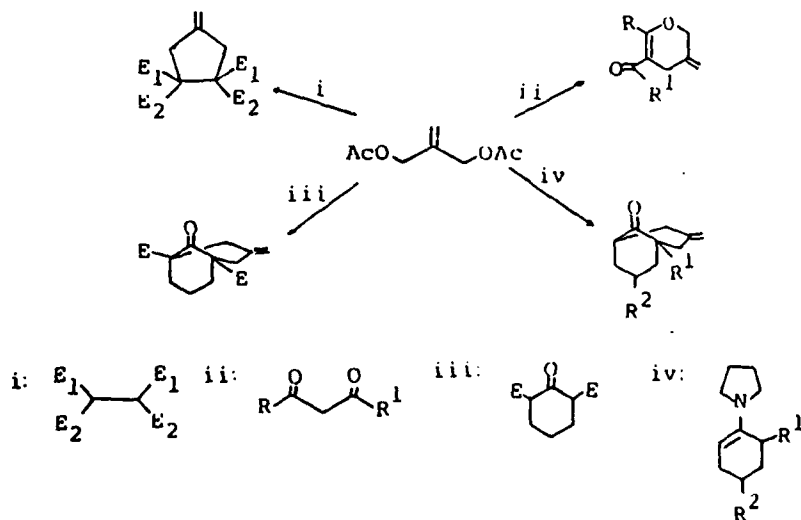
Ethyl- and 2-thienylmagnesium bromide and phenyl- and benzylzinc chloride coupled with (1) regioselectively to give the corresponding 2-substituted-4-bromoanisoles (2) in moderate to good yields.

**PALLADIUM CATALYZED ANNULATION REACTION  
USING BIFUNCTIONAL ALLYLIC ALKYLATING AGENT**

Xiyun Lu and Yujin Huang

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The reaction of 2-methylene-propane-1,3-diol diacetate (1) with  $\beta$ -diketone or  $\beta$ -ketoester bearing two active hydrogen atoms, which could react with 1 first as a carbon nucleophile then subsequently as an O-nucleophile, to give pyrane derivatives in one pot reaction is described. The usefulness of 1 as a bifunctional alkylating agent in organic synthesis also lies in preparing various types of ring compounds by the selection of different dicarbanions. In these reactions, 1 can be regarded as an  $\alpha, \alpha'$  synthon.





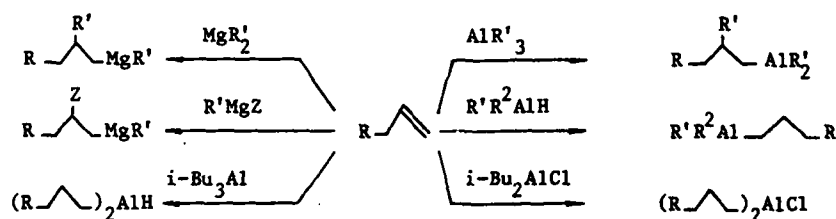
METAL COMPLEX CATALYSIS FOR THE CHEMISTRY OF  
Mg- AND Al-ORGANICS

U.M.Dzhemilev, O.S.Vostrikova, A.G.Ibragimov,  
and G.A.Tolstikov

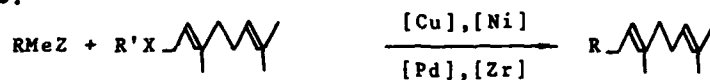
Institute of Chemistry, Bashkirian Research Centre,  
USSR Acad.Sci. Ural Department, Ufa 450054, U.S.S.R.

The paper presented covers the results obtained by the authors during recent five years in the field of employment of metal complex catalysis to develop new regio- and stereoselective synthesis techniques for Mg and Al organics.

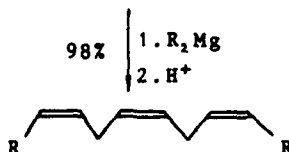
With Ti and Zr complexes taken as catalysts, the selective hydro- and carbometallations of olefins, dienes, and acetylenes have been carried out with the assistance of alkyl and hydride derivatives.



On the basis of ONCs synthesized, the effective methods of catalysis have been proposed to design new bonds as C-C, C-N, and C-S.



Me=Mg, Al; R=RC=C-; R<sub>2</sub>N-; RS-  
R-C≡C-CH<sub>2</sub>-C≡C-CH<sub>2</sub>-C≡C-R'

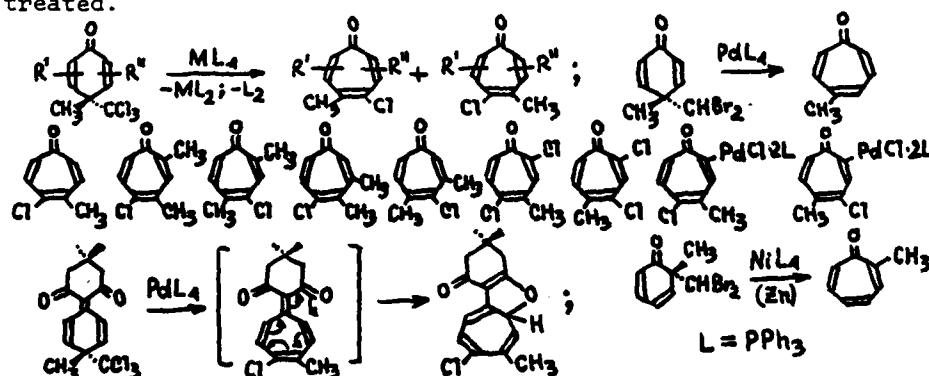


NEW ORGANOMETALLIC INTERRELATIONS BETWEEN SEMIQUINONDS  
AND NON-BENZENOID AROMATIC COMPOUNDS

V.A.Nikanorov, G.V.Gavrilova, S.V.Sergeev, V.I.Rozenberg,  
O.A.Reutov

A.N.Nesmeyanov Institute of Organo-Element Compounds of the  
Academy of Sciences of USSR, Moscow 117813, Vavilova 28, USSR

In 1984 we discovered the reaction of redox-troponization - a new effective method for inert gem-CHHal<sub>2</sub>- and -CHAl<sub>3</sub>-group activation in ortho- and para-semiquinoids under the action of low-valent transition metal complexes. This opens new organometallic route for the synthesis of hardly available tropones, heptafulvenes, their analogues and derivatives [1,2]. Some mechanistic aspects of the process as a possible combination of Ad<sub>ox</sub> M(O) into C-Hal bond, F<sub>red</sub> of α-halo-substituted organometallic intermediate, and subsequent ring expansion in homoallyl-like carbene or carbenoid will be discussed. Stereochemical differences between Pd- and Pt-induced reactions, as well as the effect of metal (Ni>Pd>Pt), halogen (Br>Cl) and semiquinoid ring substituents (H, CH<sub>3</sub>, Cl) on the rates, product ratio and toposelectivity of the ring skeletal isomerisation are also treated.



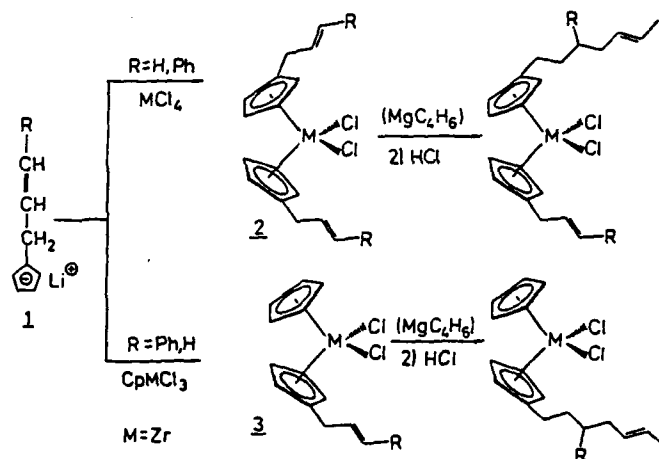
1. V.A.Nikanorov, G.V.Gavrilova, V.I.Rozenberg, O.A.Reutov, Izv. AN SSSR, ser.khim., 1984, s.2647; 1987, s.2345
2. V.I.Bakmutov, M.V.Galakhov, V.A.Nikanorov, G.V.Gavrilova, V.I.Rozenberg, O.A.Reutov, DAN SSSR, 1987, T.295, s.1376

**Reaction of Cp-substituted Metallocenedichlorides with Magnesium-Butadiene: A Method of Increasing the Chain Length of unsaturated Cp-substituents**

Rainer Aul, Gerhard Erker

Institut für Organische Chemie der Universität Würzburg  
Am Hubland, 8700 Würzburg (BRD)

The metallocene derivatives **2**, featuring unsaturated substituents at the Cp-rings were obtained by reaction of lithium salts **1** with Zirconiumtetrachloride. The mixed metallocenedichlorides **3** were obtained from the reaction of **1** with  $\text{CpZrCl}_2$ .



The Cp-substituted metallocenedichlorides **2** and **3**, when treated with magnesium-butadiene, undergo carbon-carbon coupling at the Cp-allyl group. Subsequent work-up with HCl affords a new metallocene dichloride bearing one unsaturated Cp-substituent whose chain length has been increased by four carbon atoms.

NEW C-C BOND FORMING REACTIONS OF ALKYNES WITH ALKENES AND ALLENES  
WITH PALLADIUM AND PLATINUM DIAZADIENE COMPLEXES

Christina Munz and Heindirk tom Dieck, Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13 (F.R.G.)

The sparingly soluble  $\text{Pd}(\text{dba})_2$  affords complexes  $(\text{DAD})\text{Pd}(\text{alkyne})$  1 or the palladacyclopentadienes  $(\text{DAD})\text{Pd}-\text{C}=\text{C}-\text{C}=\text{C}$  2, when reacted with DAD (diazadiene  $\text{RN}=\text{CR}'-\text{CR}'=\text{NR}$ ) and dmad (dimethyl acetylene dicarboxylate). These complexes react catalytically with various alkynes  $\text{R}^1-\text{CC}-\text{R}^2$  to give penta- ( $\text{R}^1 = \text{H}$ ) or hexasubstituted benzenes [1]. In special cases (e.g.  $\text{Ph}-\text{CC}-\text{H}$ ) not only the catalytic products of the triple bond insertion into the  $\text{Pd}-\text{C}$  bond of 2 are isolated, but also the linear products of the  $\text{C}-\text{H}$  addition to the  $\text{Pd}-\text{C}$  bond.

When 2 is reacted with terminal alkenes (e.g. 1-hexene, 1,4-hexadiene, Methoxypropadiene), palladacyclopentenes 3, postulated in the catalysis literature, are formed and are fully characterized by NMR techniques. With other alkenes such as allylic alcohols the complexes 3 are much more reactive and yield linear dienones, dienals or dienols, depending on the substitution pattern of the allylic system and the preferred  $\beta$ -elimination either from a ring or a side chain position [2]. A number of similar intermediates have also been obtained starting from  $\text{Pt}(\text{dba})_2$ . Based on the structures of the Pd and Pt complexes and the stereochemistry of the  $[2\pi + 2\pi + 2\pi]$  reaction products a general mechanism for catalytic reactions of alkynes with other  $\pi$ -systems at the  $\text{Pd}(0)$  center will be discussed.

[1] H. tom Dieck, Chr. Munz, Chr. Müller, *J. Organometal. Chem.* 326 (1987) C1.

[2] Chr. Munz, H. tom Dieck, *J. Organometal. Chem.* in preparation

AN EASY ACCESS TO  $\beta$ -ACYL AND  $\beta$ -ARYL-PROPIONALDEHYDES THROUGH A  
NEW SILYLATED ORGANOTIN HOMOEENOLATE EQUIVALENT

Jean-Baptiste Verlhac and Michel Pereyre, Laboratoire de Chimie  
Organique et Organométallique UA 35 CNRS, Université de  
Bordeaux I, 351, Cours de la libération, 33405 - Talence Cedex  
(France)

Homologation by a three-carbon reagent is a process of considerable synthetic interest and several lithiated species have been proposed as homoenolate equivalents ( $d^3$  propionaldehyde synthons). However, such highly reactive species do not tolerate various fonctionnal groups.

We had previously employed for this purpose  $\alpha$ -alkoxyallyltins<sup>1</sup> but difficulties appeared with the simplest reagent  $\alpha$ -ethoxyallyltributyltin which tends to isomerize readily into  $\gamma$ -ethoxyallyltributyltin.

We describe a fast and efficient method<sup>2</sup> to introduce the simplest homoenolate anion  $-\text{CH}_2\text{CH}_2\text{CHO}$  on acyl chlorides and aryl bromides via a new easily accessible reagent : ( $\alpha$ -methoxy- $\gamma$ -tributylstannyl)allyltrimethylsilane.

1 - J.P. QUINTARD, A. Duchêne, G. Dumartin, B. Elisondo and J.B. Verlhac, Rev. Silicon Germanium, Tin Lead, Compd., 1986, 9, 241.

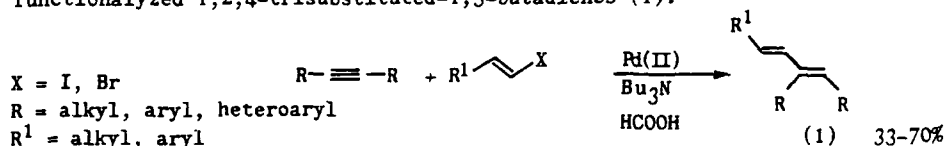
2 - J.B. Verlhac, J.P. Quintard and M. pereyre, J. Chem. Soc. Chem. Commun., in press.

PALLADIUM-CATALYSED STEREoselective HYDROVINYLATION OF DISUBSTITUTED ACETYLENES: PREPARATION OF FUNCTIONALYZED 1,2,4-TRISUBSTITUTED-1,3-BUTADIENES

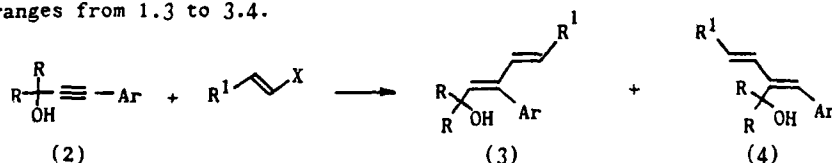
A. Arcadi<sup>a</sup>, E. Bernocchi<sup>b</sup>, A. Burini<sup>c</sup>, S. Cacchi<sup>b</sup>, F. Marinelli<sup>a</sup>, B. Pietroni<sup>c</sup>

- a) Dip. di Chimica Ingegneria Chimica e Materiali, Università degli Studi, Via Assergi 4, 67100 L'Aquila (Italy)  
 b) Dip. di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università "La Sapienza", P.le A. Moro 5, 00185 Roma (Italy)  
 c) Dip. di Scienze Chimiche, Università degli Studi, Via S. Agostino 1, 62032 Camerino (Italy)

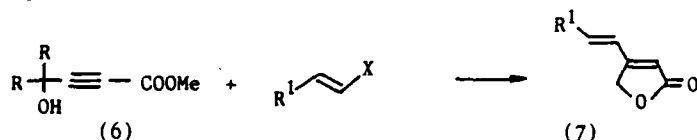
Vinyl halides have been reacted with disubstituted acetylenes in the presence of palladium-tributylammonium formate<sup>1</sup> to give stereoselectively<sup>2</sup> functionalized 1,2,4-trisubstituted-1,3-butadienes (1).



A variety of functional groups can be tolerated in the starting disubstituted acetylenes. Acetylenes disubstituted with different steric demanding groups, such as arylolethynyl, dialkylcarbinols (2)<sup>3</sup> react with moderate regioselectivity to produce the isomer (3) in higher yield. The ratio (3)/(4) ranges from 1.3 to 3.4.



Better regioselectivity was observed in the hydrovinylation of carbomethoxyethynyl, dialkylcarbinols (6). In these cases the hydrovinylation step is followed by an in situ cyclization to 3-alkenyl butenolides (7)<sup>4</sup>



- 1) Cacchi, S.; Felici, M.; Pietroni, B. *Tetrahedron Lett.* (1984) **25**, 3137. 2) Arcadi, A.; Cacchi, S.; Ianelli, S.; Marinelli, F.; Nardelli, F. *Gazz. Chim. It.* (1986) **116**, 725. 3) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron* (1985) **41**, 5121; Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* (1986) **42**, 6397. 4) Arcadi, A.; Bernocchi, E.; Burini, A.; Cacchi, S.; Marinelli, F.; Pietroni, B. *Tetrahedron* (1988) **44**, 481

**CARBON-CARBON BOND FORMATION IN CATIONIC OLEFIN CARBYL COMPLEXES  
OF PLATINUM AND PALLADIUM**

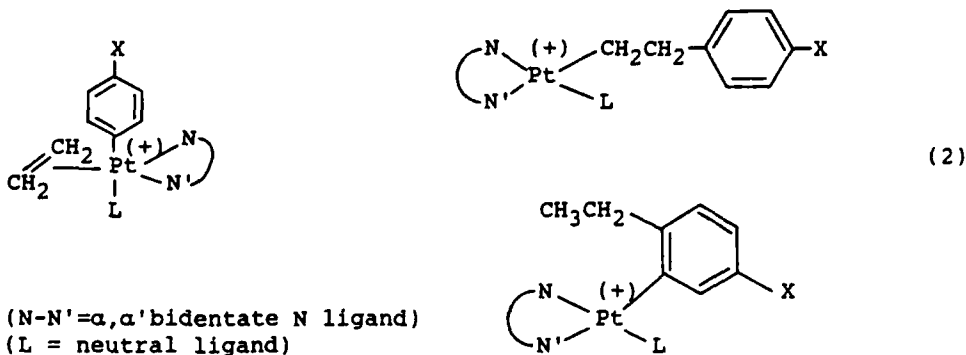
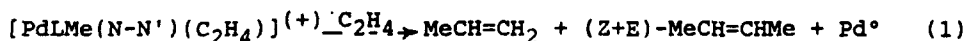
Vincenzo De Felice, Augusto De Renzi, Achille Panunzi and  
Aldo Vitagliano, Dipartimento di Chimica, Università di Napoli,  
Via Mezzocannone 4, 80134 Napoli, Italy

Five-coordinate olefin complexes of platinum(II)<sup>1</sup> and palladium(II)<sup>2</sup> containing  $\sigma$ -bonded carbon ligands have been recently described. These complexes have two important properties:

- a) They are well characterized species, with an olefin and a  $\sigma$ -bonded carbyl group occupying two adjacent coordination positions.
- b) Olefin coordination is reversible, and the free energy change of the process can be modulated by a proper choice of the ligands.

The complexes are thus ideal substrates for the investigation of possible insertion and/or related reactions involving C-C bond formation between an olefin and some other carbon ligand.

We found that neutral complexes are generally not reactive, while an interesting reactivity is displayed by cationic species. Our preliminary results are summarized in schemes 1 and 2.



Work supported by CNR and MPI

- 1) Albano, V.G.; Braga, D.; De Felice, V.; Panunzi, A.; Vitagliano, A. Organometallics 1987, **6**, 517.
- 2) De Renzi, A.; Morelli, G.; Panunzi, A.; Vitagliano, A. Gazz. Chim. Ital. 1987, **117**, 445.

NUCLEOPHILIC AROMATIC SUBSTITUTIONS IN THE ( $\eta^6$ -CHLOROBENZENE) ( $\eta^5$ -CYCLOPENTADIENYL) IRON (II) CATION

Eduardo J.S. Vichi, Joseph Miller, Paulo J.S. Moran and Paulo C.B. Gomes; Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, 13081-Campinas, SP, Brasil

Nucleophilic substitutions in halogenoarene transition metal complexes have gained synthetic importance in organic chemistry since the parent organic molecules are virtually inert to nucleophiles under normal conditions. The  $\pi$ -complexation to  $\text{Cr}(\text{CO})_3$  activates the arene ligand toward methoxide to an extent similar to the effect of a 4-nitro substituent<sup>1</sup>, although different mechanisms of electron withdrawal have been suggested for the two systems<sup>2</sup>. The effect of complexation with  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}^+$  is even more marked, being equivalent to that of ortho- and para nitro groups combined<sup>3</sup>. We report here the results of a kinetic study of the reactions of  $[(\eta^6\text{-C}_6\text{H}_5\text{Cl})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{BF}_4]$  with a varied range of nucleophiles including anionic such as  $\text{MeO}^-$ ,  $\text{PhO}^-$ ,  $\text{MeS}^-$ ,  $\text{N}_3^-$  and neutral such as morpholine, piperidine, guanidine and thiourea. For the anionic nucleophiles the reactivities increase in the order  $\text{N}_3^- < \text{PhO}^- < \text{PhS}^- < \text{MeS}^- < \text{MeO}^-$ , which neither correlate with the relative reactivities with 2,4-dinitrochlorobenzene nor with the polarizabilities of the nucleophiles. For the neutral nucleophiles the order is thiourea < aniline < morpholine < piperidine < guanidine. The differences in the reactivities of the arene complex and 2,4-dinitrochlorobenzene towards these nucleophiles are discussed in terms of the localization of the "arenide electrons", i.e. the electrons displaced from the reaction center by the nucleophile in forming the addition intermediate. In the dinitrochlorobenzene intermediate these electrons are located mainly on the ( $\beta$ -exocyclic) oxygen atoms and in the arene complex (Meisenheimer complex) they remain effectively in the ring where the attack occurs. The reactions were followed by titrating the displaced  $\text{Cl}^-$  ions with  $\text{AgNO}_3$  solutions.

1. D.A. Brown and J.R. Raju; J. Chem. Soc. A. 1960 40.
2. A.Z. Kreindlin, et al., J. Organomet. Chem. 1975, 92, 197.
3. A.N. Nesmeyanov et al., Doklady Acad. Nauk. SSSR 1968, 183, 834

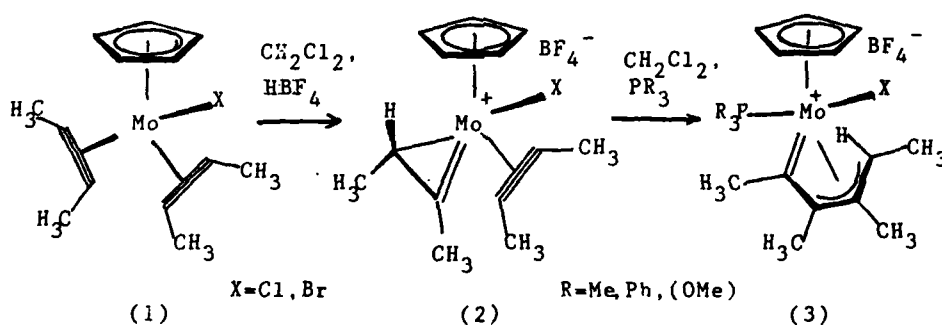


THE FORMATION OF CATIONIC  $\eta^2$ -VINYL COMPLEXES AND THE  
EVIDENCE FOR THE COUPLING OF AN  $\eta^2$ -VINYL AND ALKYNE LIGAND

Michael Green, Carolyn Reeve, Christopher Woolhouse, Department of Chemistry,  
King's College London, Strand, London. WC2R 2LS. UK.

Grainne Conole, Mary McPartlin, School of Chemistry, Polytechnic of North  
London, Holloway Road, London. N7. UK.

The molybdenum bis acetylene complexes,  $[\text{Mo}(\eta^2\text{-CH}_3\text{C}\equiv\text{CCH}_3)_2(\eta\text{-C}_5\text{H}_5)(\text{X})]$ , ( $\text{X} = \text{Br}$ , 1a;  $\text{X} = \text{Cl}$ , 1b), have been shown to be useful starting materials for the investigation of carbon-carbon coupling reactions at a metal centre. Complexes containing an  $\eta^2$ -vinyl moiety may be synthesised by the reaction of (1a) or (1b), with  $\text{HBF}_4$ . The resulting cationic species (2), was found to be reactive towards phosphines,  $\text{PR}_3$  ( $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ ) and phosphites,  $\text{P}(\text{OR})_3$ , ( $\text{R} = \text{CH}_3$ ), which leads to coupling of the  $\eta^2$ -vinyl and alkyne ligands to form an allyl carbene fragment.



The structure of (3) has been confirmed by x-ray crystallography and the mechanism of formation is discussed in relation to other allyl carbene forming processes. The further chemistry of (1), (2) and (3) is outlined, with particular reference to the deprotonation of the methyl carbene and alkyne functions.

CHARACTERIZING ORGANOMETALLIC COMPOUNDS BY SIMULTANEOUS  
ELEMENTAL ANALYSIS OF C,H,N,S, WITH THE INNOVATE CARLO  
ERBA ST. EA 1108 INSTRUMENT.

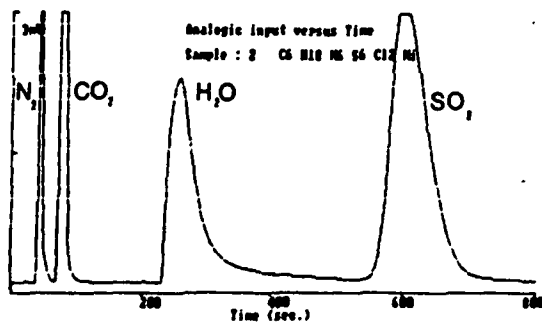
Marco Baccanti and Bruno Colombo, Carlo Erba Strumenta-  
zione, Strada Rivoltana, 20090 Rodano (Milan), Italy.

A method based on high temperature flash combustion  
followed by catalytic oxidation, reduction, gas  
chromatographic separation and detection by thermal  
conductivity is presented.

Nitrogen, carbon dioxide, water and sulphur dioxide  
are simultaneously and dynamically determined in less  
than 14 min.

N, C, H, S found weight percentages are printed out  
by a personal computer with a dedicated software.  
The analytical procedures are performed automatically  
and up to 196 samples can be analysed continuously and  
automatically.

A typical output is shown below. A series of  
experimental result obtained for a number of  
organometallic compounds will be described.



Date : 05-29-1988 Time : 11:06:31 Company name :  
Sample : 2 C6 H18 N6 S6 C12 Ni Type : Unknown  
Sample Weight : 2.028 Base Line drift (micV): 24  
Operator :

#	Ret. T.	Area (micV.s)	Area %	Comp. %	Feat. name
1	23	197	.004		
2	43	70876	12.588	16.88023	Nitrogen
3	75	168408	29.911	14.72409	Carbon
4	256	121287	21.542	3.642198	Hydrogen
5	595	202251	35.922	38.69496	Sulphur

Carb./Hyd. Area = 1.386508 Carb./Nitr. Area = 2.376093  
Carb./Sulp. Area = .322668

SYNTHESIS AND REACTIVITY OF HYDROQUINONE  
CHROMIUM TRICARBONYL COMPLEXES

Hans Schumann, Atta M. Arif and Thomas G. Richmond, Department of Chemistry,  
University of Utah, Salt Lake City, Utah 84112 (USA)

Chromium tricarbonyl complexes of the general type  $(\eta^6\text{-aren}(\text{OSi}(\text{CH}_3)_3)_2)\text{Cr}(\text{CO})_3$  (aren =  $\text{C}_6\text{H}_2\text{R}'_2$ : 1a  $\text{R}'_2 = \text{H}_2$ , 1,4 -  $(\text{OSiR}_3)_2$ ; 1b  $\text{R}'_2 = 2,5 - (\text{t-C}_4\text{H}_9)_2$ , 1,4 -  $(\text{OSiR}_3)_2$ ; 1c  $\text{R}'_2 = 3,5 - (\text{t-C}_4\text{H}_9)_2$ , 1,2 -  $(\text{OSiR}_3)_2$ ; and aren =  $\text{C}_{10}\text{H}_6$ : 1d 1,2 -  $(\text{OSiR}_3)_2$ ) have been obtained from the thermal CO substitution in  $\text{Cr}(\text{CO})_6$  by bis(trimethylsilyl) - protected hydroquinones. The molecular structure of complex 1d was determined by X-ray structure analysis and will be discussed in comparison with related structures of substituted naphthalene chromium tricarbonyl complexes.

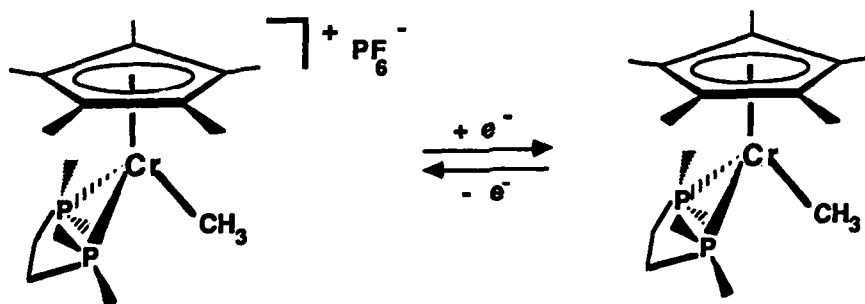
Deprotection of the  $\text{Si}(\text{CH}_3)_3$  protection groups in complexes 1 by  $\text{F}^-$  under controlled conditions give the related hydroquinone complexes 2 in high yield. Further deprotonation by selected bases afford the dianionic complexes 3,  $(\eta^6\text{-aren}(\text{O}^-)_2)\text{Cr}(\text{CO})_3$ .

Selected reactions and properties for the complexes 1 to 3 will be presented in comparison with related hydroquinone complexes. Based on spectroscopic data, the change of electron density on the  $\text{Cr}(\text{CO})_3$  unit will be analysed with respect to the observed lability of some of the coordinated arene ligands. Possible applications for these complexes will also be outlined.

REDOX CHEMISTRY AND SMALL MOLECULE ACTIVATION WITH  
PARAMAGNETIC CHROMIUM ALKYLs

Barbara J. Thomas, Darrin S. Richeson, Klaus H. Theopold, Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853, USA.

A great variety of paramagnetic alkyl complexes of chromium(III) have been prepared in our laboratory and their reactivity has been investigated. More recently, we have used these compounds as starting materials for chromium alkyls in other oxidation states (see below for an example).



The products of reductions as well as oxidations of several Cr(III) precursors will be described. The reactions of these new compounds with small molecules (e.g. alkenes) will also be discussed.

OXIDATIVE ELECTROCHEMISTRY OF THE COMPOUNDS  
[MCp<sub>2</sub>HX] (M=Mo(IV); W(IV), X=H,Cl,Br,SMe).

A.R. Dias, M. Helena Garcia, M. Paula Robalo and C.C. Romão  
Centro de Química Estrutural, I.S.T. 1096 Lisboa Codex.

The oxidative electrochemistry of the compounds [MCp<sub>2</sub>X<sub>2</sub>] (M=Mo(IV), W(V); X=halide or thiolate, had been examined previously (1), by cyclic voltammetry and coulometry. In order to explore the electrochemical behaviour of this general family of compounds and to understand their reactivity we have extended these studies to the compounds [MCp<sub>2</sub>HX] (X=H,Cl,Br,SMe), which results we report on this communication.

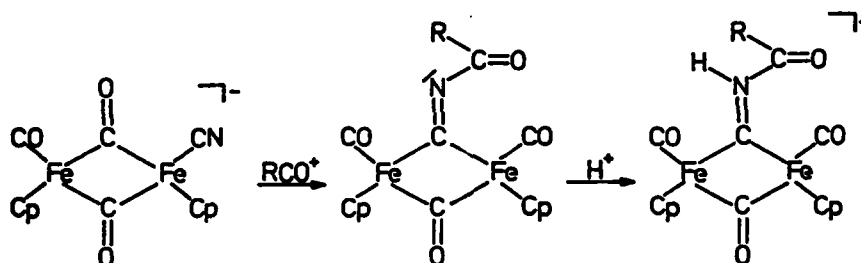
- (1) J.C. Kotz, W. Vining, W. Coco, R. Rosen, A.R. Dias and M.H. Garcia  
Organometallics, 68-79 (1983).

## ACYLISOCYANIDE METAL COMPLEXES

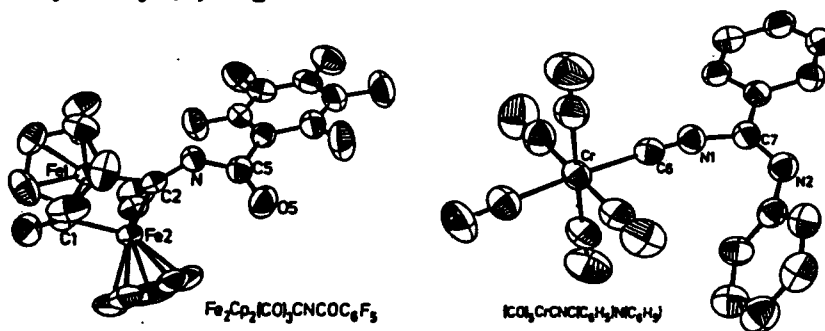
A. Schröder and W.P. Fehlhammer

Institut für Anorganische und Analytische Chemie der Freien  
Universität Berlin, D-1000 Berlin 33 (West-Germany)

Treatment of cyanometallate anions with acyl- and iminoacyl halides represents a simple approach to functional isocyanide complexes. Terminal acylisocyanide complexes are mild acylating agents, which also add to multiple bonds (e.g. in  $R_2N-C\equiv C-Ph$ ). By acylation of the dinuclear cyanoiron species  $[Fe_2Cp_2(CO)_3CN]^-$ , a variety of new isocyanide bridged compounds has been obtained, which can further be protonated and alkylated.



The spectroscopic properties (ir, nmr, ms, uv) of the compounds will be discussed. Some of their structures have been ascertained by x-ray analysis, e.g.

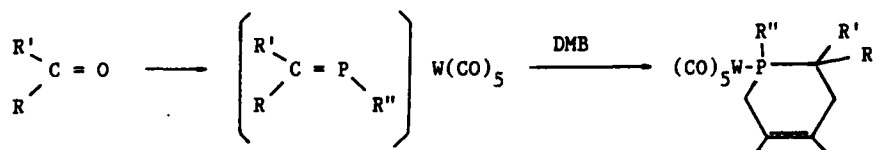


## A NEW SYNTHESIS OF PHOSPHAALKENES-W(CO)<sub>5</sub> COMPLEXES

Angela Marinetti-Mignani and François Mathey, Laboratoire de Chimie du Phosphore et des Métaux de Transition.  
Ecole Polytechnique, 91128 Palaiseau Cedex, France.

Unhindered phosphalkene-  $W(CO)_5$  complexes are generated at low temperature from carbonyl compounds.

Cycloaddition with DMB is used as trapping reaction to allow an easy characterization of the most unstable complexes.



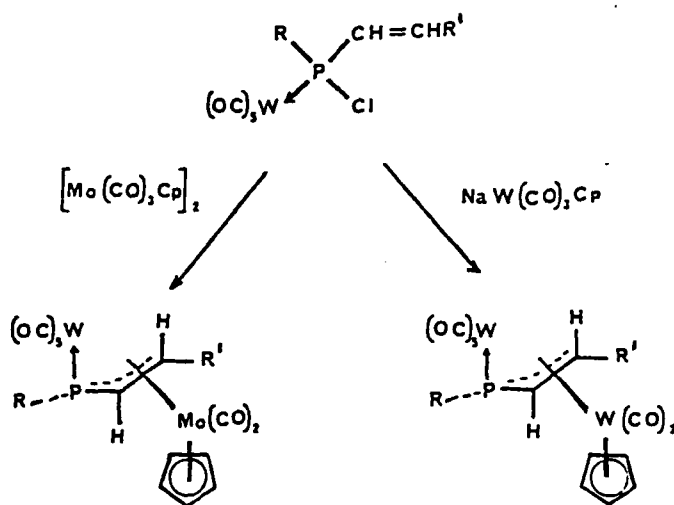
SYNTHESIS OF  $\eta^3$ -PHOSPHAALLYL-MOLYBDENUM  
AND TUNGSTEN COMPLEXES.

François Mercier, Catherine Hugel-Le Goff and François Mathey, Laboratoire DCPH  
Ecole Polytechnique, 91128 Palaiseau Cedex, France

During the last few years numerous phosphorous analogues of classical transition metal  $\pi$ -complexes have been described in the literature. In this order we have recently described the synthesis and chemical properties of one new type of the class, i.e. the  $\eta^3$ -1-phosphaallyl iron complexes (1).



We wish to report here after the synthesis of  $\eta^3$ -1-phosphaallyl-molybdenum and tungsten analogues :



Some aspects of their reactivity will be presented.

(1) F. Mercier, C. Hugel-Le Goff, F. Mathey. Organometallics to be published.

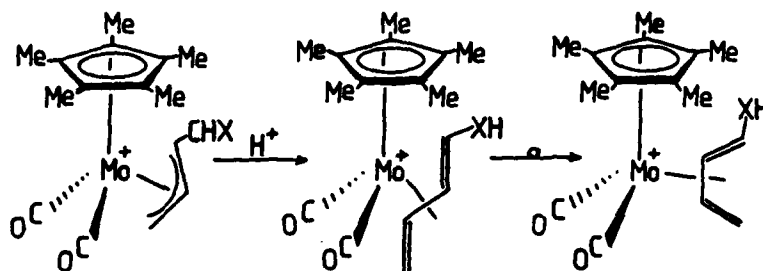


SYNTHESIS AND PROTONATION OF SUBSTITUTED  $\eta^3$ -ALLYL COMPLEXES OF MOLYBDENUM;  
EVIDENCE FOR THE INTERMEDIACY OF CATIONIC TRANSOID  $\eta^4$ -1,3-DIENE SPECIES

Stephen A. Benyunes, Michael Green, Michael J. Grimshire, Stanley C. Nyburg,  
and Adrian W. Parkins, Department of Chemistry, King's College London,  
Strand, London. WC2R 2LS. UK.

The cationic molybdenum acetonitrile complex  $[\text{Mo}(\text{NMe})_2(\text{CO})_2(\text{Cp})]^+[\text{BF}_4]^-$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_7$ ,  $\eta^5\text{-C}_5\text{Me}_5$ ), reacts with 1-methoxy-1,3-cyclohexadiene, yielding the corresponding diene complex. Treatment of the latter with NaOMe results in a facile demethylation, with the isolation in high yield of a neutral oxo-substituted allyl complex. A direct synthesis can likewise be accomplished by the use of 1-trimethylsiloxy-1,3-cyclohexadiene *via* a fluoride-induced desilylation. Similarly, the use of the appropriate acyclic diene allows the preparation of the allyl-aldehyde complex  $[\text{Mo}(\eta^3\text{-CH}_2\text{-CH-CH-CHO})(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_5)]$  [1], which has been characterised by x-ray diffraction. Upon treatment with the Wittig reagent  $\text{Ph}_3\text{PCH}_2$ , complex [1] undergoes selective attack at the aldehyde centre affording the methylene-allyl complex [2].

Complexes [1] and [2] are protonated readily by the strong acids  $\text{HBF}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$  affording the cationic diene complexes [3] and [4]. Low temperature n.m.r. studies demonstrate the initial adoption by the diene of a transoid conformation, followed by an irreversible isomerisation to the more stable cisoid species (scheme).



[1],[3],  $\text{X} = \text{O}$

[2],[4],  $\text{X} = \text{CH}_2$

NEW ORGANOMETALLIC RHENIUM COMPLEXES CONTAINING  
THE ANIONIC FAC-TRIPOD ORGANOMETALLIC LIGAND  
[ $\eta\text{-C}_5\text{H}_5\{\text{P}(\text{O})(\text{OEt})_2\}_3\text{]}^-$  ( $\text{R} = \text{C}, \text{CH}_3$ )

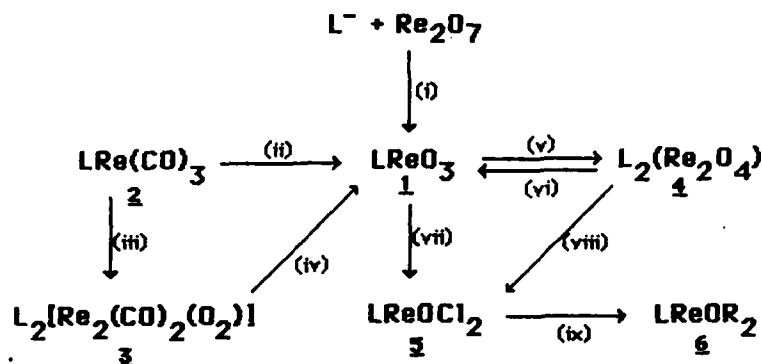
Enrique Román<sup>1</sup>, Sergio Hernández<sup>1</sup>, Fernando Tapia<sup>1</sup> and Alan H. Cowley<sup>2</sup>.

<sup>1</sup>Facultad de Química. Pontificia Universidad Católica de Chile. P.O.Box 6177.

Santiago-Chile. <sup>2</sup>Department of Chemistry. University of Texas at Austin.

Texas, Austin-78712. United States.

A series of new mono and polynuclear rhenium complexes in low and high oxidation states have been synthesized. In all of them the anionic fac-tripod ligand  $\text{L}^- = [\eta\text{-C}_5\text{R}_5\{\text{P}(\text{O})(\text{OEt})_2\}_3]^-$  ( $\text{R} = \text{H}, \text{CH}_3$ ) is facially coordinated to the rhenium metal center. The synthetic route can be described by the scheme.



(i) THF, r.t.; (ii), (iii), (iv)  $h\nu$ ,  $\text{O}_2$ ; (v) oxo-abstraction by  $\text{PR}_3$ ;  
(vi)  $\text{O}_2$ ; (vii)  $\text{PR}_3$ ,  $\text{HCl}$ ; (viii)  $\text{HCl}$ ; (ix)  $(\text{CH}_3)_3\text{CCH}_2\text{Li}$ , THF.

X-ray diffraction studies for the 1, 2 and 5 rhenium complexes were carried out. Distortional and electronic effects produced by the anionic  $\text{L}^-$  ligand were correlated with spectroscopical properties. Complexes 6 showed to be potential model for olefine metathesis catalysts *via* the obtained alkylidene complexes 6.

## NEW IRON(II) THIOLATES CONTAINING NITROGEN-DONOR LIGANDS.

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G. Gervasio, Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Italy

T. Hoffmann, Inorganic Chemistry Division, Humboldt University, Berlin, GDR

Absorption of CO under mild conditions is a useful and convenient method for the preparation of thiolato iron(II) carbonyls from solutions of Fe(II) salts containing the necessary ligands and a base. The compounds synthesized by this method all contain a two-electron donor S-, N-, or P- ligand in addition to the thiolato and CO groups.

Using the same method, several new iron(II) carbonyl complexes containing thiolato and N-donor ligands were prepared.

Two types of complexes were synthesized and characterized: complexes of type **A** with the general formula  $\text{Fe}(\text{S}^-\text{N})_2(\text{CO})_2$  where (S<sup>-</sup>N) represents a ligand containing a thiolato and an amino group; and complexes of type **B** having the general formula  $\text{Fe}(\text{SPh})_2(\text{N}^-\text{N})(\text{CO})_2$  which contain a bidentate N-ligand (N<sup>-</sup>N).

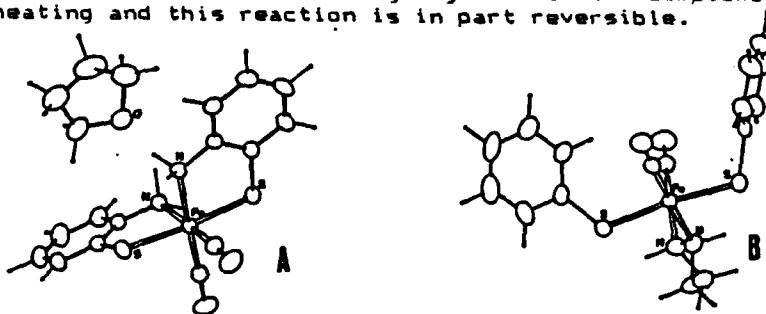
The structures of two representatives were determined by X-ray analysis:  $\text{Fe}(\text{SC}_6\text{H}_4\text{NH}_2-o)_2(\text{CO})_2$  for type **A** and  $\text{Fe}(\text{SPh})_2(\text{H}_2\text{NC}_2\text{H}_4\text{NH}_2)(\text{CO})_2$  for type **B** (Fig.).

According to the IR spectra the octahedral complexes contain two CO ligands in *cis* position, while the coordinated N atoms are *trans* to the CO groups.

Both molecules possess a C<sub>2</sub> symmetry in the solid state, the twofold axis lying between the two CO and the two NH<sub>2</sub> groups. However, only the molecule of type **A** remains chiral in solution (owing to the configuration of the chelate rings about the iron atom); the chirality of molecule **B** in the crystal is only due to the conformation of the chelate ring and will be lost if the compound is dissolved in a solvent.

Complex **A** crystallizes with one molecule of tetrahydrofuran linked via hydrogen bonds N-H...O to the complex, while the complex molecules are enchainned via weak N-H...S bonds.

A necessary condition for the stability of such complexes is the presence of at least one chelating ligand: all the complexes loose CO on heating and this reaction is in part reversible.



PREPARATION AND CHEMISTRY OF CYCLOPENTADIENYLIRON BIS(PHOSPHANE)  
LIGAND CATIONS CONTAINING GROUP IVb TO VIb LIGANDS

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Universität Heidelberg, D-6900 Heidelberg 1 (FRG)

Arnold L. Rheingold, Department of Chemistry, University of Delaware,  
Newark, Delaware 19716 (USA)

The photochemical substitution of the coordinated arene ligand in  $[\text{C}_5\text{H}_5\text{Fe}(\eta^6\text{-p-(CH}_3)_2\text{C}_6\text{H}_4)]\text{PF}_6$  in acetonitrile solution in the presence of two equivalents of phosphanes  $\text{PR}_3$  afford complexes of the general type  $[\text{C}_5\text{H}_5\text{Fe}(\text{PR}_3)_2(\text{NCCH}_3)]\text{PF}_6$  in high yield and purity. Due to the lability of the coordinated nitrile ligand, substitution reactions with donor/ akzeptor ligands containing group IVb to VIb centers afford electronrich complexes of the type  $[\text{C}_5\text{H}_5\text{Fe}(\text{PR}_3)_2(\text{L})]\text{PF}_6$  in high yield.

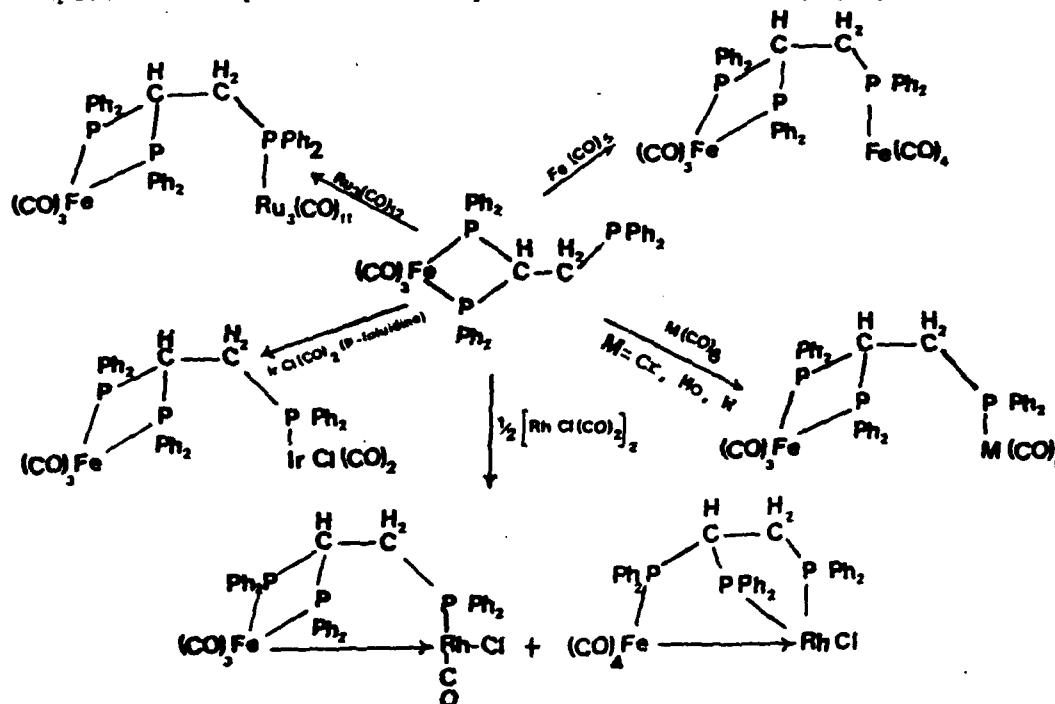
The reactivity of selected complexes towards ligand displacement and modification of the coordinated ligand will be reported together with the results of spectroscopic investigations including X-ray structure analysis. Obtained results and spectroscopic trends will be discussed in comparison with related investigations in the  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{L})]\text{BF}_4$  series.

THE SYNTHESIS OF HETEROMETALLIC COMPLEXES BY USE OF  
MULTIDENTATE PHOSPHINE LIGANDS

Nagwa Nawar and Anthony K. Smith, Department of Inorganic, Physical and Industrial Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England.

It has been shown<sup>1</sup> that the coordinated ligand  $\text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2$  readily undergoes Michael addition type reactions. We have made use of this reaction to synthesise "dangling" phosphine complexes of the type  $[\text{M}(\text{CO})_n\{\eta^2-(\text{Ph}_2\text{P})_2\text{CHCH}_2\text{PPh}_2\}]$  which provide convenient

starting materials for the synthesis of heteronuclear metal complexes. Examples of such complexes are illustrated below:



The syntheses and spectroscopic characterisation of these complexes will be described, together with some of their subsequent thermal rearrangements.

Reference

1. See for example, A.M. Herring, S.J. Higgins, G.B. Jacobsen and B.L. Shaw, J. Chem. Soc. Chem. Commun., 1986, 882.

PHOTOCHEMISTRY OF  $M(CO)_3(R-DAB)$  ( $M=Fe, Ru$ ), A GROUP OF COMPLEXES WITH TWO CLOSE-LYING REACTIVE EXCITED STATES.

Derk J. Stufkens, Hans K. van Dijk and Ad Oskam, Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

The complexes  $M(CO)_3(R-DAB)$  ( $M=Fe, Ru$ ;  $R-DAB=1,4$ -diaz-1,3-butadiene) possess an intense metal to ligand charge-transfer (MLCT) band in the visible region. Irradiation into this band at room temperature in the presence of a nucleophile causes photosubstitution of CO. Flash photolysis shows that this reaction can proceed via loss of CO or by breaking of a Fe-N bond, depending on the substituent R.

When the complexes  $Fe(CO)_3(R-DAB)$  with not too bulky substituents R are, however, irradiated into the MLCT band in n-pentane at 150K, a wavelength dependent photochemistry is observed. Irradiation at the high-energy side of the band causes loss of CO and formation of a dimer  $Fe_2(CO)_5(R-DAB)_2$ . A completely different photoproduct,  $Fe(CO)_3(\eta^4-R-DAB)$  is formed upon irradiation at lower energy. In this latter complex the R-DAB ligand has obtained a novel  $\eta^4$ -coordination. Raising the temperature to 200K causes a backreaction of this photoproduct to the starting complex.

Under similar conditions the complexes  $Ru(CO)_3(R-DAB)$  only show the formation of the dimer  $Ru_2(CO)_5(R-DAB)_2$  at all wavelengths of irradiation, whereas the substituted complexes  $Ru(CO)_2(R-DAB)(PR_3)$  only produce the  $\eta^4$ -coordinated R-DAB photoproduct  $Ru(CO)_2(\eta^4-R-DAB)(PR_3)$ . The occurrence of these two, completely different, photochemical reactions is explained in terms of an energy diagram with close-lying reactive  $^3LF$  and  $^3MLCT$  excited states.<sup>1</sup>

#### References

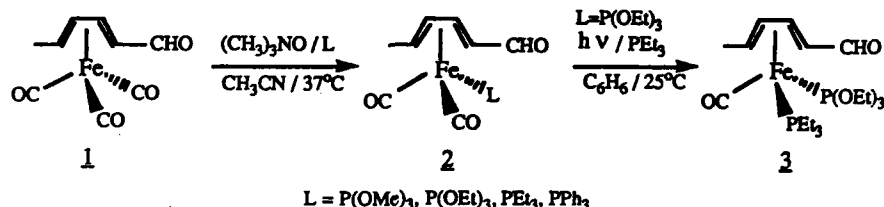
- 1) H.K. van Dijk, D.J. Stufkens and A. Oskam, submitted for publication.

**SYNTHESIS, STRUCTURE AND CONFORMATIONAL ANALYSIS  
OF CHIRAL ( $\text{Fe}(\text{CO})\text{L}_1\text{L}_2(\eta^4\text{-DIENE})$ ) COMPLEXES.**

I. Solana, C.M. Adams, S. Chimichi, A. Hafner and W. von Philipsborn

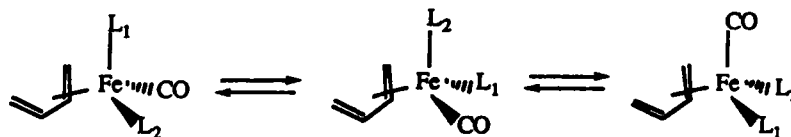
Organisch-Chemisches Institut der Universität Zürich, CH-8057 Zürich  
(Switzerland)

A versatile method for selective and stepwise carbonyl displacement in acyclic ( $\text{Fe}(\text{CO})_3(\text{diene})$ ) and ( $\text{Fe}(\text{CO})_3(\text{enone})$ ) complexes by phosphane or phosphite ligands is described. The reactions are applicable to alkyl-substituted and functionalized 1,3-dienes, for example, the sorbic aldehyde complexes **1** and **2**:



Complexes of type **2** exhibit planar chirality (racemate), those of type **3** a chiral iron centre and a chirality plane (two racemic diastereoisomers). The molecular structure of the predominant racemic diastereoisomer of **3** was determined by X-ray diffraction.

In solution, complexes of type **1**, **2** and **3** are fluxional:

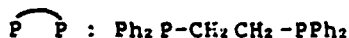
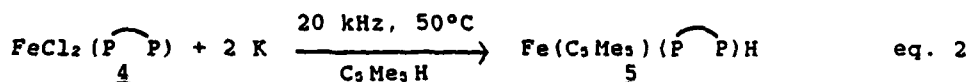
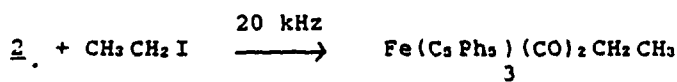
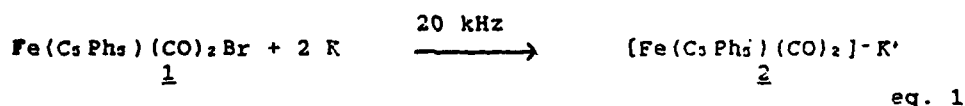


and show temperature-dependent  $^{13}\text{C}$ -,  $^{17}\text{O}$ - and  $^{31}\text{P}$ -NMR spectra. The conformational isomers and their relative population were assigned at 180-200K based on  $^{13}\text{C}$  and  $^{31}\text{P}$  chemical shifts and  $^2\text{J}(\text{P},\text{P})$  and  $^2\text{J}(\text{P},\text{C})$  spin coupling data. The structural and spectroscopic results indicate a pronounced stereochemical preference of the iron ligands depending upon ligand size and diene substitution.

## SONOCHEMICALLY PROMOTED ACCESS TO NEW ORGANO IRON COMPLEXES.

Patrick Brégaïnt, Christophe Roger, Jean-René Hamon  
and Claude Lapinte, Laboratoire de Chimie des Organométalliques,  
UA CNRS 415, Université de Rennes I, 35042 Rennes Cedex, France.

The high intensity ultrasound is a powerful tool in organometallic synthesis. It allows the use of stoichiometric amount of activated reducing reagent (i.e. colloidal potassium) which improved the chemistry of the formed highly reactivity species. It enhances the reactivity of insoluble transition metal complexes such as  $[\text{Fe}(\text{C}_5\text{Ph}_5)(\text{CO})_2]\text{-K}^+$  and it also can be used for generation of transient zerovalent transition metal intermediates like metal vapor chemistry. These properties are illustrated by the equations 1 and 2 which shown the synthetic interest of ultrasound to develop new reactions.

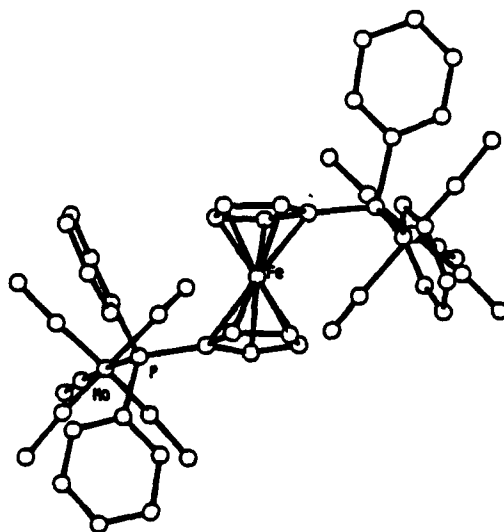




1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE AS A BRIDGING LIGAND IN  
HETEROBINUCLEAR ORGANOMETALLIC COMPLEXES

Olli Orama and Jukka Hietala, Department of Inorganic Chemistry,  
University of Helsinki, Vuorikatu 20, SF-00100 Helsinki, Finland

In recent papers we have studied binuclear diphosphine-bridged complexes formed by bis(diphenylphosphino)acetylene and  $L_nM$  ( $L_nM = Cp(CO)_2Mn$ ;  $(CO)_5Cr$ ;  $(CO)_5Mo$ ;  $(CO)_5W$ ). In this work we use ferrocene instead of acetylene to yield heterobimetallic trinuclear complexes with the hope to get complexes with unusual catalytic properties. The preparation of transition metal complexes of type  $[Fe(C_5H_4PPh_2)_2][L_nM]_2$  using organothallium compounds as intermediates is described. The compounds are fully analyzed and the crystal structure of bis[ $\eta^5$ -(pentacarbonyl-molybdenum)diphenylphosphinocyclopentadienyl]iron has been determined from X-ray diffraction data.

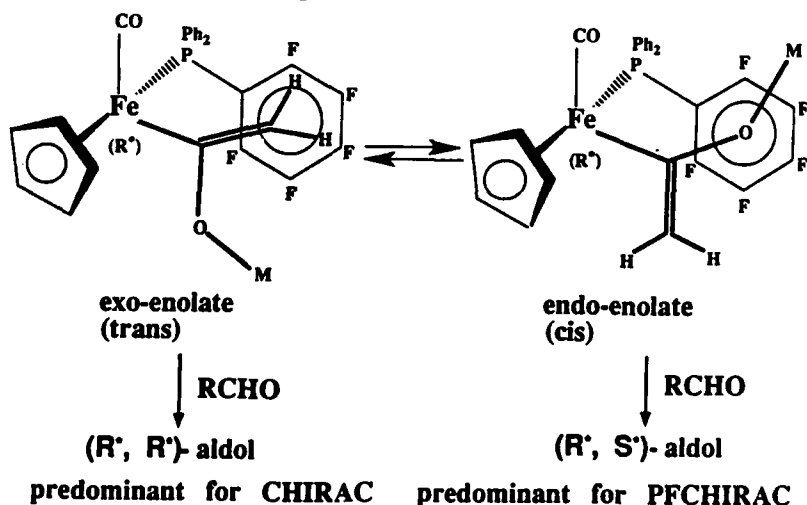


**Remarkable Effects of a Pentafluorophenyl Group on the  
Stereoselective Reactions of a Chiral Iron Acyl Complex**

Iwao Ojima and Hyok Boong Kwon

Department of Chemistry, State University of New York  
at Stony Brook, Stony Brook, New York 11794, U.S.A.

A novel chiral iron acyl complex,  $[(C_6F_5)Ph_2P](CO)CpFe-COMe$  (PFCHIRAC), is synthesized. The stereoselective aldol and imine condensation reactions with benzaldehyde and benzylidenedianiline using the lithium, tin, aluminum, and copper enolates of PFCHIRAC are studied. The reactions give  $(R^*, S^*)$ -products regardless of the metal enolate species with high stereoselectivities (89 - 99% d.e.). The observed unique stereo-differentiation is rationalized based on an electron donor - acceptor type attractive interaction between the pentafluorophenyl moiety and the enolate oxygen. The variable temperature NMR ( $^1H$ ,  $^{19}F$ ,  $^{31}P$ ) study of the dynamic behavior of PFCHIRAC strongly supports the rationale.

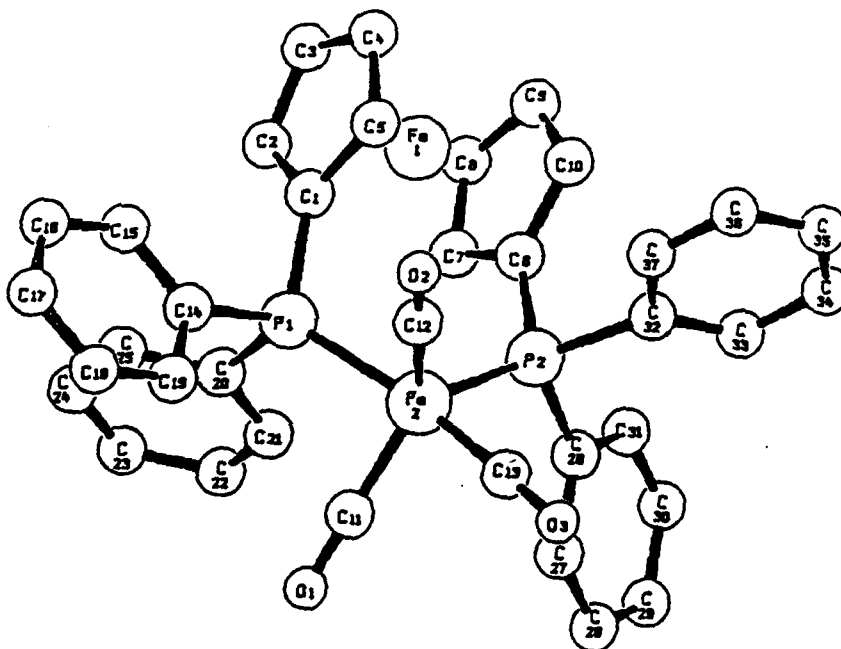


SYNTHESIS AND STRUCTURE OF  
(1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE)TRICARBONYLIRON(0),  
(FDPP)Fe(CO)<sub>3</sub>

Ling-Kang Liu\*, Show-Kei Yeh, and Chu-Chieh Lin  
Institute of Chemistry, Academia Sinica  
Nankang, Taipei, Taiwan 11529 ROC

(Fdpp)Fe(CO)<sub>3</sub> has been prepared by the reaction of 1,1'-bis-(diphenylphosphino)ferrocene and (maleic acid)tetracarbonyl-iron(0) as firstly attacked by trimethylamine-oxide. The structure of (fdpp)Fe(CO)<sub>3</sub> has been studied with ir, nmr, and x-ray diffraction.

Crystals of (fdpp)Fe(CO)<sub>3</sub> crystallize in the monoclinic space group P2<sub>1</sub>/c with cell constants a 9.710(3), b 16.162(9), c 19.910(5) Å, and β 95.78(2) deg. The x-ray diffraction studies have resulted in a final R 0.036 for 2416 reflections. The two cyclopentadienyl moieties are staggered. The coordination geometry around the tricarbonyl Fe is a distorted trigonal bipyramid with one P occupying the equatorial site and the other P axial. The P-Fe-P angle is 99.88(7) deg. The ferrocenyl Fe still holds its sandwiched position. There is no direct Fe-Fe interaction.

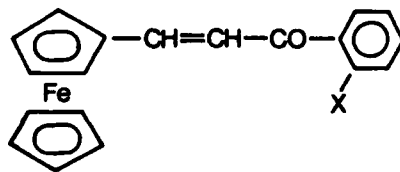


FERROCENES STUDIED BY  $^{13}\text{C}$  NMR AND CYCLIC VOLTAMMETRY

Ágnes G. Nagy, Chemistry Department, Central Research  
Institute for Physics, 1121 Budapest, Hungary

Pál Sohár, EGIS Pharmaceuticals, Spectroscopic Department,  
POB 100, 1475 Budapest, Hungary

Ferrocene analogues of chalcone substituted in the ortho position /1/ were prepared and investigated by  $^{13}\text{C}$  NMR and cyclic voltammetry. The change in the oxidation potential of the ferrocenyl group and the changes of the electron densities at the carbon atoms in the molecules caused by the substituents are presented and the intramolecular interactions are discussed. A comparison of these effects in the ortho- and para-substituted series is also given.

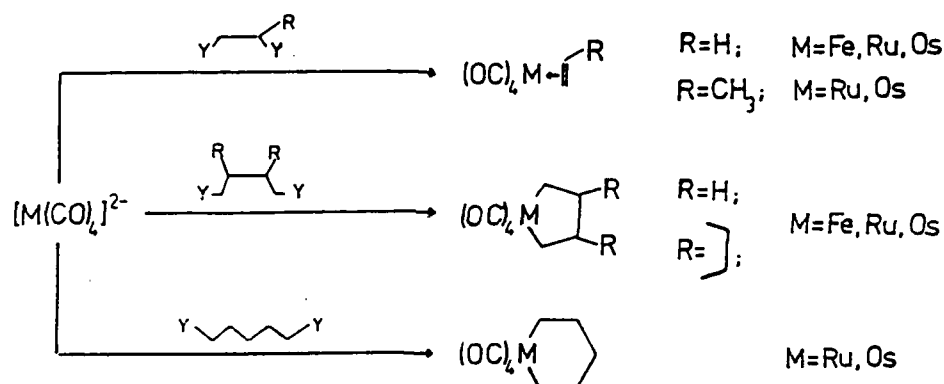


### A Simple Route to Ruthena- and Osmacycloalkanes

Rolf-Michael Jansen and Ekkehard Lindner\*, Institut für Anorganische Chemie der Universität, Auf der Morgenstelle 18, D-7400 Tübingen, West-Germany

For lack of suitable synthetic methods, only few mononuclear carbonyl complexes of the iron triad, containing metall-carbon- $\sigma$ -bonds, are known. By using the nucleophilic elimination cycloaddition method we found a simple route to these systems<sup>1,2</sup>.

Reaktion of  $[M(CO)_4]^{2-}$  ( $M = Fe, Ru, Os$ ) with  $\alpha, \omega$ -alkanediyl-bis(trifluoromethanesulfonates) yields three- to six-membered metallacycles.



The ring systems show the expected reactivity. Thermal decomposition results in the formation of the corresponding alkenes and alkadienes. Formal insertion of CO in one of the M-C bonds, followed by reductive elimination of the metal fragment, yields cyclic ketones.

#### References:

- 1) E. Lindner, E. Schauf, W. Hiller and R. Fawzi, *Angew. Chem. Int. Ed. Engl.* **23**, 711 (1984).
- 2) E. Lindner, R.-M. Jansen and H. A. Mayer, *Angew. Chem. Int. Ed. Engl.* **25**, 1003 (1986).

Alkene Complexes of Ruthenium(0): Photochemical  
Alkene Hydrogenation

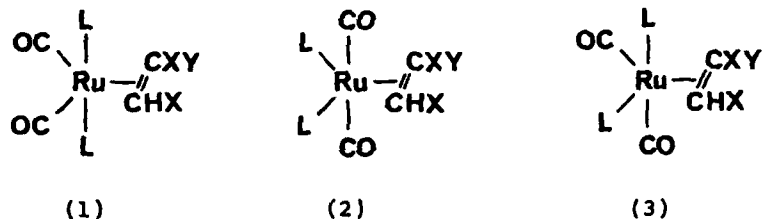
Jonathan Vessey, Michael Whittlesey and Roger Mawby

Department of Chemistry, University of York, York YO1 5DD, England

We have prepared alkene complexes of ruthenium(0),  
[Ru(CO)<sub>2</sub>(CHX=CXY)(PMe<sub>2</sub>Ph)<sub>2</sub>], where X = CO<sub>2</sub>Me or CN, Y = H or Cl:

- (i) by rearrangement of vinyl hydride complexes  
[Ru(CO)<sub>2</sub>(CX=CXY)H(PMe<sub>2</sub>Ph)<sub>2</sub>],
- (ii) by displacement of H<sub>2</sub> from [Ru(CO)<sub>2</sub>H<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>],
- (iii) by displacement of ethene from [Ru(CO)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>].

Detailed n.m.r. studies have indicated three stereochemistries for these complexes (shown below, where L = PMe<sub>2</sub>Ph):



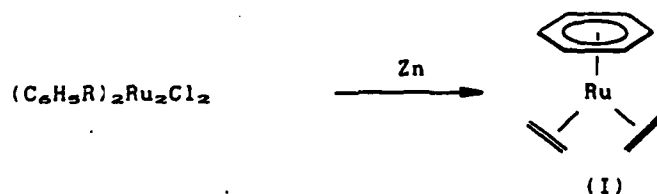
The relative energies of (1), (2) and (3), and the energy barriers for their interconversion, appear to be very sensitive to the nature of X and Y.

We are currently studying the photochemical reactions of the alkene complexes and their vinyl hydride precursors. In C<sub>6</sub>D<sub>6</sub> solution and in the absence of free H<sub>2</sub>, [Ru(CO)<sub>2</sub>(CH(CO<sub>2</sub>Me)=CH(CO<sub>2</sub>Me))(PMe<sub>2</sub>Ph)<sub>2</sub>] yields the hydrogenated product MeO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me under irradiation, with concurrent formation of a new organo-ruthenium complex.

## REACTIONS OF ARENE-RUTHENIUM BISOLEFIN COMPLEXES

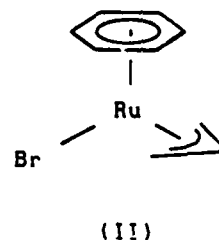
Richard S. Bates and Anthony H. Wright, Department of Chemistry,  
University of Nottingham, Nottingham, NG7 2RD, U.K.

Arene ruthenium bisolefin complexes (I) can be made in high yield utilising low-temperature ultrasound. The reaction appears to be general for different types of aromatic and for a range of different olefins. The scope of the reaction will be described.



These complexes are highly reactive, undergoing both substitution and oxidative addition reactions. When simple CO substitution reactions are carried out, products involving arene loss are isolated. However with other substitution reactions, complexes of the form (arene)RuL<sub>2</sub> may be isolated.

The bisolefin complexes are particularly suitable for oxidative addition reactions that generate four-electron donor ligands. Thus the addition of allylbromide generates the new series of air sensitive complexes (arene)RuBr(allyl) (II). These and other products of oxidative addition reactions will be described.



**COMPARATIVE STUDY OF THE BIDENTATE PHOSPHINE LIGANDS  
BIS(DIPHENYLPHOSPHINO)METHANE (DPPM) AND  
1,1-BIS(DIPHENYLPHOSPHINO)ETHENE (DPPEE)  
WITH COMPLEXES OF METAL CARBONYLS**

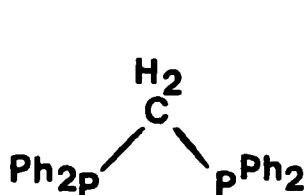
RICHARD H. DAWSON AND ANTHONY K. SMITH

DEPARTMENT OF INORGANIC, PHYSICAL AND INDUSTRIAL CHEMISTRY,  
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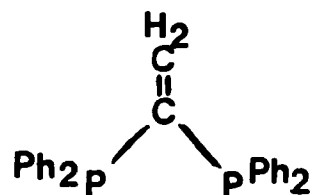
THE USE OF MULTIDENTATE PHOSPHINE LIGANDS TO STABILISE AND TO PROVIDE SITES OF REACTIVITY IN HOMO- AND HETERO- METALLIC SPECIES IS WELL KNOWN.

STUDIES COMPARING AND CONTRASTING SUCH LIGANDS ARE RARE. WE REPORT A COMPARATIVE STUDY OF BIS(DIPHENYLPHOSPHINO)METHANE AND 1,1-BIS(DIPHENYLPHOSPHINO)ETHENE IN REACTIONS WITH MONO-, BI- AND TRI-METALLIC COMPLEXES OF IRON, RUTHENIUM, OSMIUM AND RHODIUM.

EXAMPLES OF SOME OF THE COMPLEXES TO BE DISCUSSED INCLUDE:  
 $\text{Fe}(\text{CO})_3(\text{L-L})$ ,  $\text{M}_3(\text{CO})_9(\text{L-L})_2$  ( $\text{M} = \text{Ru}$  AND  $\text{Os}$ ) AND  
 $\text{Rh}_2(\mu\text{-CO})\text{Cl}_2(\text{L-L})_2$ .



**DPPM**



**DPPEE**



REACTIVITY PATTERNS OF DINUCLEAR DIPHOSPHAZANE LIGAND BRIDGED  
DERIVATIVES OF COBALT

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of South Africa.

Dinuclear diphosphazane ligand bridged derivatives of cobalt of the type  $[\text{Co}_2(\text{CO})_4(\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2)_2]$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^i$ ) are electron-rich and, as such, are susceptible to electrophilic attack. Reactions with  $\text{I}_2$ ,  $\text{CBr}_4$  and  $\text{CCl}_4$  in toluene lead to loss of CO and formation of the halogeno-bridged species  $[\text{Co}_2(\mu\text{-X})(\mu\text{-CO})(\text{CO})_2(\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2)_2]^+$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^i$ ;  $\text{X} = \text{I}, \text{Br}$  or  $\text{Cl}$ ). These cations are readily reduced by  $\text{BH}_4^-$  to afford essentially two neutral products which spectroscopic measurements indicate to be  $[\text{Co}_2(\text{CO})_4(\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2)_2]$  and the dihydrido species  $[\text{Co}_2\text{H}_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2)_2]$ . Reaction of  $[\text{Co}_2(\text{CO})_4(\mu\text{-(MeO)}_2\text{PN(Et)P(OMe)}_2)_2]$  with  $\text{CCl}_4$  in methanol (rather than toluene) in the presence of  $\text{BPh}_4^-$  gives the salt  $[\text{Co}(\text{CO})_2\{\text{P(OMe)}_2\}_2\{\text{(MeO)}_2\text{PN(Et)P(OMe)}_2\}] [\text{BPh}_4]$  as confirmed X-ray crystallographically. Significantly, the cation is mononuclear with two  $\text{P(OMe)}_2$  ligands, as well as a pendant diphosphazane ligand, bonded to the cobalt atom. Presumably, the  $\text{P(OMe)}_2$  ligands derive from chlorine radical attack at the phosphorus atom of a diphosphazane ligand resulting in fission of the P-N bond and formation of  $\text{P(OMe)}_2\text{Cl}$ ; the latter is then attacked by methoxide ions to give the  $\text{P(OMe)}_2$  ligand. Protonation of  $[\text{Co}_2(\text{CO})_4(\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2)_2]$  using  $\text{HPP}_6$  in methanol, or even methanol alone, proceeds rapidly and quantitatively to give the bridged hydrido species  $[\text{Co}_2(\mu\text{-H})(\text{CO})_4(\mu\text{-(RO)}_2\text{PN(Et)P(OR)}_2)_2]^+$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^i$ ) the structure of the  $\text{BPh}_4^-$  salt having been determined X-ray crystallographically.

SYNTHESIS AND REACTIVITY OF VINYLIDENE-, KETENIMIN-  
AND AZACARBENE(RHODIUM)-COMPLEXES

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The paper describes the synthesis of monomeric, halfsandwich-type vinylidene(rhodium) compounds  $(C_5H_5)(PPr_3^1)Rh(=C=CHR)$  with bulky and strongly electron withdrawing substituents at the vinylidene ligand ( $R=tBu$ ,  $CO_2CH_3$ ).

Via cycloaddition reactions of these compounds with organic azides ( $R'N_3$ ), the corresponding  $\eta^2-N,C$  ketenimin complexes  $[Z]-(C_5H_5)(PPr_3^1)RhC(CHR)N(R')$  are obtained which are useful precursors for cyclic azacarbene(rhodium) derivatives  $[(C_5H_5)-(PPr_3^1)RhC(CH_2R)N(R')]BF_4$ . In addition, a stereoselective  $\eta^2-N,C$  to  $\eta^2-C,C$  rearrangement of the ketenimin(rhodium) compounds will be reported.

## BIMETALLIC RHOIUM (I) COMPLEXES OF FLUORINATED THIOLATE LIGANDS.

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The syntheses and characterization of new rhodium (I) bimetallic compounds of the type  $[\text{Rh}(\mu\text{-SRf})(\text{COD})]_2$  are presented. The complexes were prepared by metathetic reaction of  $[\text{Rh}(\mu\text{-Cl})(\text{COD})]_2$ , where COD = cyclooctadiene, with  $\text{M}(\text{SRf})_n$  where  $\text{M} = \text{Pb}$ ,  $n = 2$  and  $\text{SRf} = \text{p-HC}_6\text{F}_4\text{S}^-$ ,  $\text{p-FC}_6\text{H}_4\text{S}^-$ ,  $\text{C}_6\text{F}_5\text{S}^-$  or  $\text{M} = \text{Ag}$ ,  $n = 1$  and  $\text{SRf} = \text{CF}_3\text{S}^-$ . Because of the relevance of these species to a number of catalytic processes, their reactivity pathways towards triphenylphosphine and carbon monoxide has been examined in detail, establishing significant differences that can be related to the basicity of the fluorinated pseudohalides and of the (phosphine/dimer) ratio employed. The complexes  $[\text{Rh}(\mu\text{-SRf})(\text{CO})_2]_2$ ;  $[\text{Rh}(\mu\text{-SRf})(\text{P}\phi_3)(\text{CO})_2]$ ;  $[\text{Rh}(\text{SRf})(\text{P}\phi_3)(\text{CO})_2]$  and  $[\text{Rh}(\text{SRf})(\text{P}\phi_3)(\text{COD})]$  were isolated.

These compounds were characterized by the usual spectroscopic techniques, the molecular "bend" structures of  $[\text{Rh}(\mu\text{-SC}_6\text{F}_5)(\text{COD})]_2$ ,  $[\text{Rh}(\mu\text{-SC}_6\text{F}_4\text{H})(\text{COD})]_2$  and  $[\text{Rh}(\mu\text{-SC}_6\text{H}_4\text{F})(\text{CO})_2]_2$  as shown by X ray diffraction will be discussed.

A preliminary study of the behavior of the complexes  $[\text{Rh}(\mu\text{-SRf})(\text{COD})]_2$  on olefine hydrogenation reactions is also presented.

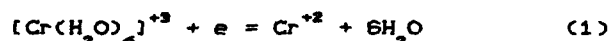
VOLTAMMETRIC BEHAVIOUR OF  $[\text{Cr}(\text{HCOOH})]^{+2}$ 

J. Szynekarczuk, I. Drela, J. Kubicki

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 Technical University of Wrocław, Wybrzeże Wyspiańskiego 27,  
 50-370 Wrocław, POLAND

Electrochemical reduction of the complex cations  $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$  and  $[\text{Cr}(\text{HCOO})]^{+2}$  in 0.5 M solution of sodium perchlorate (supporting electrolyte) was investigated.

Voltammetric behaviour of prepared complex indicates that at pH = 4.0 there are two cathodic peaks corresponding to the following processes:



It was noticed that with the increase of the scan rate, peaks potentials move towards more negative values. Cyclic voltammetry of  $[\text{Cr}(\text{HCOO})]^{+2}$  on hanging mercury drop electrode shows that there are no anodic peak corresponding to the cathodic ones. Anodic process:  $\text{Cr}^{+2} + 6\text{H}_2\text{O} = [\text{Cr}(\text{H}_2\text{O})_6]^{+3} + e$  is observable in the values ca -0.40 V (referred to Ag/AgCl electrode). These experimental facts prove that reduction of cations is totally irreversible in both cases.

Some electrokinetic parameters were calculated:

	reaction (1)	reaction (2)	dimension
transfer coefficient	0.42	0.59	
Tafel coefficient	0.14	0.10	V
peak potential (v=0.1 V/s)	-1.15	-1.47	V
half-peak potential	-1.18	-1.41	V
diffusion coefficient	$6.5 \cdot 10^{-6}$	$3.3 \cdot 10^{-6}$	$\text{cm}^2/\text{s}$
standard rate constant	$4.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$\text{cm/s}$
(calc. at half-peak potential)			

THE MECHANISM OF OXIDATION OF 2-HYDROXYCYCLOHEXYL RADICAL TO  
CYCLOPENTANECARBALDEHYDE BY COPPER IONS IN AQUEOUS SOLUTIONS.

Mohammed Masarwa, Haim Cohen and Dan Meyerstein

Nuclear Research Centre Negev, R. Bloch Coal Research Center and  
Chemistry department Ben-Gurion University of the Negev, Beer-Sheva.

Copper ions are known to change the reaction course of the oxidation of cyclohexene by peroxydisulphate. It has been suggested that this change is due to the selective oxidation of 2-hydroxycyclohexyl radicals by copper(II) to yield cyclopentanecarbaldehyde. We decided to study the detailed mechanism of this reaction by the pulse-radiolysis technique.

2-Hydroxycyclohexyl radicals, produced by the addition of hydroxyl free radicals to cyclohexene, were reacted with  $\text{Cu}^{2+}_{\text{aq}}$  and  $\text{Cu}^{+}_{\text{aq}}$  ions in aqueous solutions. Surprisingly enough it was found that  $\text{Cu}^{2+}_{\text{aq}}$  ions react only slowly with the free radicals. On the other hand  $\text{Cu}^{+}_{\text{aq}}$  react with 2-hydroxycyclohexyl radicals with a rate approaching the diffusion controlled limit. The product of the latter reaction, (I), rearranges in a process obeying a first order rate law into a second short lived intermediate, (II). The absorption spectrum of (II) indicates that the copper-carbon bond was maintained in the rearrangement process. The intermediate (II) decomposes in a process obeying a first order rate law to form the final products. The rate of both first order processes is independent of  $[\text{Cu}^{2+}_{\text{aq}}]$  and  $[\text{Cu}^{+}_{\text{aq}}]$ . Cyclopentanecarbaldehyde is quantitatively formed in this reaction sequence. A detailed mechanism for these reactions is proposed and discussed.

## ORGANOMETALLIC PHOTOCHEMISTRY IN SUPERCRITICAL FLUIDS

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and John M. Whalley  
Department of Chemistry, University of Nottingham,  
Nottingham, England NG7 2RD

Supercritical fluids have exciting advantages over conventional solvents as media for photochemical processes, particularly those involving reactions between gases and relatively involatile materials. Supercritical Xe ( $T_c$  16.9°C,  $P_c$  59 atm.) has the added benefit of total spectroscopic transparency from far ultra-violet to far infra-red. Unfortunately, the high pressures associated with supercritical fluids have prevented their use outside highly specialised laboratories. However, many of the hazards of working with high pressure gases are reduced greatly by use of a cell with a very small internal volume.

In this poster, we describe the construction of such a miniature high pressure cell for spectroscopy and photochemistry in supercritical fluids close to room temperature. The stainless steel cell (internal volume <1ml,  $CaF_2$  windows) has maximum operating pressure of 250 atm. and a maximum temperature of 100°C. The cell is magnetically stirred and can be used with fluids such as Xe,  $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$  and  $SF_6$ .

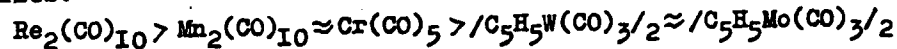
We illustrate the use of the cell by describing the photochemical reactions of transition metal carbonyl complexes with  $H_2$  which generate complexes containing "non-classical"  $\eta^2-H_2$  ligands. Such complexes are often thermally unstable but we have already shown that their lifetimes can be extended by increased pressures of  $H_2$  [1]. The effect is particularly dramatic in supercritical Xe because the concentration of dissolved  $H_2$  is much higher than in a conventional solvent under similar conditions. We present results of kinetic and spectroscopic measurements on compounds such as (n-toluene) $Cr(CO)_2(H_2)$  or (n- $C_5H_5$ ) $Mn(CO)_2(H_2)$ . These compounds are stabilised sufficiently in supercritical fluids to be studied at temperatures in excess of 80°C with a conventional IR spectrometer.

- [1] RK Upmacis, GE Gadd, M Poliakoff, MB Simpson, JJ Turner, R Whyman and AF Simpson, J. Chem. Soc. Chem. Commun. (1985) 27.

REACTIVITY OF THE TRANSITION METAL CARBONYLS IN THE SUBSTITUTION REACTIONS WITH CARBON-HALOGEN AND ELEMENT-HYDROGEN BOND FISSION.

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EPR-spectroscopy has been applied to determine rate constants of halogen abstraction from R-Hal (R=alkyl, allyl, aryl) by metal carbonyl radicals  $\text{Re}(\text{CO})_5$ ,  $\text{Mn}(\text{CO})_5$ ,  $\text{C}_5\text{H}_5\text{W}(\text{CO})_3$ ,  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3$  and coordinatively unsaturated  $\text{Cr}(\text{CO})_5$ -particles. In accordance with the rate constant values of halogen abstraction from mono-, di-, tri- and polyhalogen containing compounds found the reactivity of metal carbonyls in the substitution reaction proceeding with carbon-halogen bond rupture increases in the series:



Halogen containing compounds replacing each other, a symbatic change of rate constants of halogen abstraction for different acceptors studied was observed.

The rate constants of hydrogen abstraction from triethylsilane were determined by the analogous procedure and the following order of metal carbonyls activity in  $(\text{C}_2\text{H}_5)_3\text{Si}$ -radicals generation is displayed:



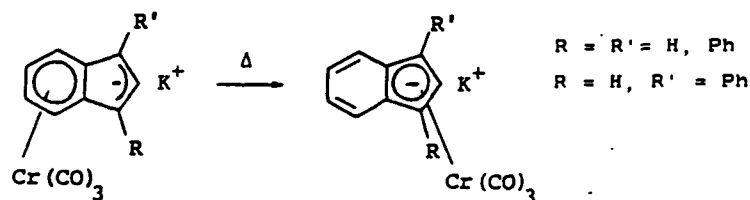
THE MIGRATION OF THE  $\text{Cr}(\text{CO})_3$  GROUP FROM THE SIX- TO THE FIVE-MEMBERED RING IN SOME POTASSIUM INDENYLS IN THF.

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The  $\eta^6 \rightarrow \eta^5$  haptotropic migration occurring in the  $\text{Cr}(\text{CO})_3$  complexed fluorenyl anion has received much attention in the near past <sup>1</sup>. In contrast, despite a theoretical study on the *iso*-lobal cyclopentadienyl-iron complex <sup>2</sup>, no experimental details have been published up today for the  $\text{Cr}(\text{CO})_3$  migration in the indenyl system.

In this communication we report the generation, the IR and the <sup>1</sup>H NMR spectra of some  $\eta^6$ -(R,R'-indenyl)- $\text{Cr}(\text{CO})_3$  anions in THF. At  $T > 253 \text{ K}$  the  $\text{Cr}(\text{CO})_3$  group migrates from the six- to the five-membered ring:



The kinetics have been followed by both <sup>1</sup>H NMR and IR spectroscopies, and the data obtained suggest that the haptotropic rearrangement occurs through a peripheral pathway.

<sup>1</sup> A.Ceccon, A.Gambaro, A.Venzo, V.Lucchini, T.E.Bitterwolf, J.Shade, J.Organometal.Chem., 327(1987)55 and ref. therein

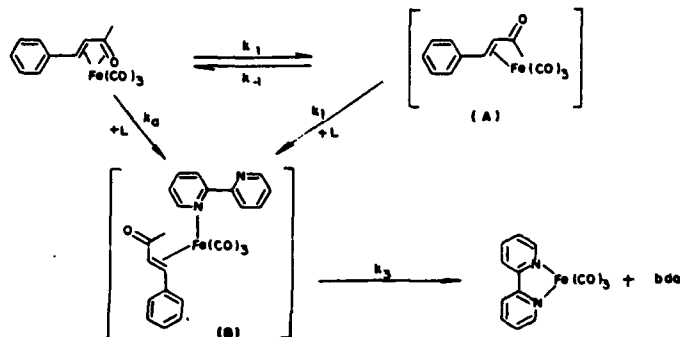
<sup>2</sup> T.A.Albright, et al., J.Amer.Chem.Soc., 105(1983)3396



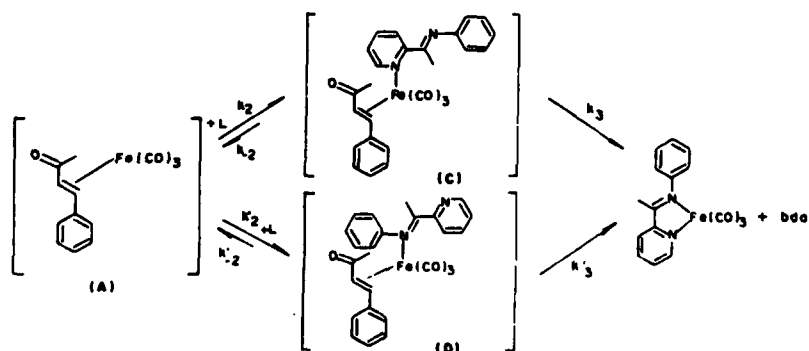
KINETICS OF THE BENZYLIDENEACETONE (bda) LIGAND SUBSTITUTION IN THE  
 $[\text{Fe}(\text{bda})(\text{CO})_3]$  COMPLEX BY DIIMINES

Edison Stein, Fatima Squizani Livotto and Eduardo J.S. Vichi, Instituto de Química, Universidade Estadual de Campinas, C.P. 6154 - Campinas, SP, Brazil

The kinetics and mechanism of the benzylideneacetone substitution in the title complex by 2,2'-bipyridyl and 2-acetylpyridineanil have been studied. The reactions were followed by I.R. spectroscopy by monitoring the sharpest  $\nu_{\text{C=O}}$  band of the  $\text{Fe}(\text{CO})_3$  group in both the reagents and products. The mechanism depends on the incoming ligand. For bipy, the reaction occurs via two concurrent paths, an associative (Id) and a dissociative (D):



For the assymmetric 2-acetylbiopyridineanil, only the dissociative path is observed. Both nitrogen atoms of the incoming ligand can bind to the 16-electrons intermediate (A) leading to intermediates C and D:



The kinetics results and the mechanism will be discussed in terms of the electronic and steric properties of the attaching ligands.

## ADDITION OF ACRYLONITRILE TO ANIONIC TRANSITION METAL HYDRIDES

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(b) Dipartimento di Chimica, Università "La Sapienza", I-00185 Roma, Italy.

The insertion of olefins into transition metal-hydrogen bond - a reaction postulated as an intermediate step in catalytic processes involving chemical modification of olefins (1) - may be investigated with suitable model reactions. The reactivity of  $\text{HCr}(\text{CO})_5^- \text{PPN}^+$  indicated a predominant hydride transfer character with polar organic substrates (2) and therefore it was a promising system for investigating the behaviour of selected alkenes.

$\text{PPN}^+ \text{HCr}(\text{CO})_5^-$  added to acrylonitrile used in excess, in THF as the solvent, at room temperature, and under a nitrogen atmosphere, to yield  $\text{PPN}^+ \text{CH}_3\text{CH}(\text{CN})\text{Cr}(\text{CO})_5^-$  (3) quantitatively.

Some acrylonitrile oligomers were isolated, but blank experiments ruled out the possibility that the addition product is an intermediate in the polymerization process.

A radical process can be excluded, on the basis of the lack of any CIDNP effect. A dissociative process is ruled out by the results of studies on  $^{13}\text{CO}$  exchange. At 22°C,  $^{13}\text{CO}$  does not exchange with  $\text{PPN}^+ \text{HCr}(\text{CO})_5^-$  in THF, either in the absence or in the presence of acrylonitrile, in the time period necessary for the  $\text{MH}^-/\text{alkene}$  reaction to occur.

Second-order kinetics and activation parameters are more consistent with an associative process. The reactivity order of a series of substituted alkenes,  $\text{CH}_2=\text{CH}-\text{CO}_2\text{CH}_3 > \text{CH}_2=\text{CH}-\text{CN} > \text{CH}_2=\text{CH}-\text{CONH}_2 \gg \text{Ph}_2\text{CH}=\text{CH}_2, \text{CH}_2=\text{CHOCOCCH}_3$  (no reaction) is in agreement with a reaction affected by electronic substituent effects on the alkene  $\beta$ -position, thus indicating hydride transfer in the rate-determining step. This hypothesis is supported by the high reactivity of  $\text{HCr}(\text{CO})_5^-$  with acrylonitrile, when the latter compound is  $\pi$ -coordinated to the  $\text{Fe}(\text{CO})_4$  moiety.

Work supported by the National Science Foundation (Grant No. CHE 8603664 to MYD).

1. J. Halpern, *Science*, **217**, 401 (1982) and references therein.
2. M. Y. Darensbourg et al., *J. Amer. Chem. Soc.*, **107**, 2428 (1985).
3. M. Y. Darensbourg, B. Floris, and K. A. Youngdahl, submitted for publication.

STUDY OF ORGANOMETALLIC COMPOUNDS USING AN IMPROVED  
VERSION OF MOLDRAW GRAPHIC PROGRAM

By P. Ugliengo, G. Borzani & G. Gervasio, Dip. di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Univ. di Torino, D. Viterbo, Dip. di Chimica, Univ. della Calabria, Rende (Cosenza), Italy.

MOLDRAW<sup>1</sup> is a program for the graphical manipulation of molecules on personal computers, with no requirement of any non standard hardware. The new features, which have recently been introduced in the program, also thanks to the suggestions of several users, are:

- Use of the coordinate files previously retrieved from the Cambridge Crystallographic Data Base through a simple interface program.
- Faster algorithm to generate the unit-cell content.
- Generation of the neighboring molecules around a given fragment or molecule.
- Adjustable vertical clipping.
- View along the normal to the least-squares plane.
- Stereo red and green view.
- Interactive keyboard controlled labelling of selected atoms for both geometrical calculations and deletion of atoms to generate a fragment.
- Display of the crystallographic atomic labels.
- Interactive keyboard control for continuous rotation along the three principal axes.
- Update of the Buckingham potential parameters for energy calculations.
- Four different ways of displaying van der Waals surface.
- Enantiomorph generation.
- Access to DOS commands without leaving MOLDRAW.

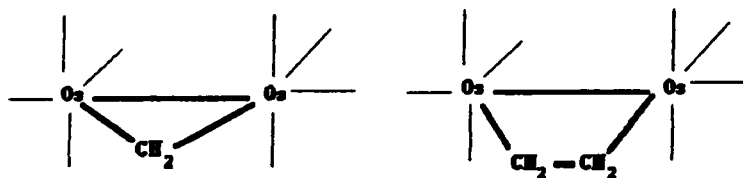
MOLDRAW proved to be extremely useful to study the structural features of mono and polynuclear organometallic compounds. Some selected examples will be shown during the present meeting.

<sup>1</sup> Ugliengo et al., J.Appl.Cryst.(1988), 21, 75.

# **UV PE Spectra and Electronic Structure of 1,2-Diosmacyclopropane and 1,2-Diosmacyclobutane Complexes.**

by Gaetano Granozzi, Renzo Bertoncello  
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Padova (Italy),  
Maurizio Casarin,  
Istituto di Chimica dell'Università della Basilicata, Potenza (Italy),  
Bruce R. Bender, Jack R. Norton  
Department of Chemistry, Colorado State University, Fort Collins (USA)  
Michael R. Burke and Josef Takats,  
Department of Chemistry, University of Alberta, Edmonton (Canada).

The electronic structures of two isolobal analogues of cyclopropane and cyclobutane,  $\text{Os}_2(\text{CO})_8(\mu\text{-CH}_2)$  and  $\text{Os}_2(\text{CO})_8(\mu\text{-C}_2\text{H}_4)$ , (see below) have been investigated by means of gas-phase UV photoelectron (PE) spectroscopy and Discrete Variational  $X\alpha$  MO calculations.



From a comparison between the bonding schemes of the organic and organometallic partners it appears that the "isolobal analogy" reproduces the gross features of the bonding of these molecules but is an oversimplification when a detailed description is attempted. Actually, when both complexes are compared with their organic analogues, the complexes have an additional framework MO with significant Os-C antibonding character. Such a distinct feature is due to the involvement of the  $t_{2g}$ -like MOs of the metallic fragment into the interactions within the dimetallacycle. The UV-PE data agree well with the picture arising from the theoretical calculations.

## Energetics of Intermediates and Reactions Steps Involved in the Hydroformylation Reaction Catalyzed by $\text{HCo}(\text{CO})_4$ . A Theoretical Study Based on the HFS-Method

Louis Versluis and Tom Ziegler

Department of Chemistry, University of Calgary  
Calgary, Alberta, CANADA

The coordinatively unsaturated hydrido-carbonyl  $\text{HCo}(\text{CO})_3$ , as well as the acyl system  $\text{CH}_3(\text{O})\text{CCo}(\text{CO})_3$  and the olefin  $\pi$ -complex  $\text{HCo}(\text{CO})_3(\text{olefin})$  are all postulated intermediates in the hydroformylation reaction, yet little is known experimentally about their structures. We have carried out unconstrained geometry optimizations<sup>1</sup> on all three systems and for each of the three intermediate determined the structures and relative stabilities of all possible conformers. We have found that  $\text{HCo}(\text{CO})_3$  as its most stable conformation has a butterfly structure with the hydride in the axial position whereas the preferred geometry for  $\text{CH}_3(\text{O})\text{CCo}(\text{CO})_3$  is a butterfly dihapto structure with the acyl-group in an equatorial position. Geometry optimizations will also be presented for  $\text{HCo}(\text{CO})_4$ ,  $\text{CH}_3\text{Co}(\text{CO})_4$  and the formyl complexes  $\text{H}(\text{O})\text{CCo}(\text{CO})_3$  and  $\text{H}(\text{O})\text{CCo}(\text{CO})_4$ .

The reaction profiles for the migratory insertion reactions



as well as the olefin insertion reaction



has been traced by a linear transit procedure and reaction enthalpies as well as activation barriers evaluated for the processes in Eq.(1) and Eq.(2). It will in particular be shown that the migratory insertion reaction (1) with  $\text{R}=\text{H}$  is unfavorable on thermodynamic as well as kinetic grounds.

<sup>1</sup> L.Versluis and T.Ziegler, J.Chem.Phys 1988

## Thermal Stability and Kinetic Lability of the M-CO Bond. A Theoretical Study Based on Density Functional Theory.

Tom Ziegler and Vincenzo Tschinke  
Department of Chemistry, University of Calgary  
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Thermochemical data on the M-CO bond, even in basic metal carbonyls such as  $M(CO)_6$  ( $M=Cr, Mo, W$ );  $M(CO)_5$  ( $M=Fe, Ru, Os$ ) and  $M(CO)_4$  ( $M=Ni, Pd, Pt$ ) are still lacking, and it is not known with certainty how the M-CO bond strength changes through a series of homologous  $M(CO)_n$  complexes made up of metals from the same triad.

We have carried out near quantitative calculations on the intrinsic mean bond energy<sup>1</sup>  $D(M-CO)$  of  $M(CO)_n$  as well as the first CO dissociation energy  $H(M-CO)$  for  $M(CO)_6$  ( $M=Cr, Mo, W$ );  $M(CO)_5$  ( $M=Fe, Ru, Os$ ) and  $M(CO)_4$  ( $M=Ni, Pd, Pt$ ). We find for both  $D(M-CO)$  and  $H(M-CO)$  the order first row > third row > second row through a triad. This trend will be rationalized in terms of steric and electronic factors as well as relativistic effects. An assessment will also be given of the conflicting experimental M-CO bond strength.

<sup>1</sup>Bond energy between M in its  $d^n$  valence state and  $n$  CO ligands.

THE SEVEN TOPOLOGICALLY DISTINCT SIX-VERTEX POLYHEDRA  
IN METAL CARBONYL CLUSTER CHEMISTRY

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There are seven topologically distinct six-vertex polyhedra, namely the octahedron, the bicapped tetrahedron, distinct  $C_3$  and  $C_{2v}$  six-vertex polyhedra having one quadrilateral face and six triangular faces, the pentagonal pyramid, a  $C_2$  six-vertex polyhedron having two quadrilateral and four triangular faces, and the trigonal prism. All of these polyhedra can be shown to play a role in metal carbonyl cluster chemistry. Metal carbonyl clusters based on the octahedron generally exhibit globally delocalized bonding consisting of a six-center core bond as well as surface bonding derived from pairwise overlap of the surface orbitals delocalized throughout the surface leading to a skeletal bonding manifold that may be regarded as topologically homeomorphic to the sphere. Metal carbonyl clusters based on the other six-vertex polyhedra as well as a few metal octahedral clusters exhibit edge-localized bonding consisting of two-center bonds along each of the polyhedral edges. Many examples of octahedral metal carbonyl clusters are known such as  $M_6(CO)_{16}$  ( $M=Co, Rh, Ir$ ) and  $Co_6C(CO)_{13}^{2-}$ . An important example of a bicapped tetrahedral metal carbonyl cluster is  $Os_6(CO)_{18}$ . The reactions of alkynes with  $RPFe_3(CO)_{10}$  derivatives lead to various  $PC_2Fe_3$  clusters based on the pentagonal pyramid, the  $C_3$  six-vertex polyhedron, and the  $C_2$  six-vertex polyhedron. An important example of a trigonal prismatic metal carbonyl cluster is  $Co_6C(CO)_{15}^{2-}$ . The remaining six-vertex polyhedron, namely the  $C_{2v}$  polyhedron having one quadrilateral face and six triangular faces, is a topologically required intermediate in the reduction of bicapped tetrahedral  $Os_6(CO)_{18}$  to octahedral  $Os_6(CO)_{18}^{2-}$ .

Gale transformations can be used to map the vertices of six-vertex polyhedra onto the circumference and the center of a unit circle without losing essential topological information. Six-vertex polyhedral rearrangements can thus be depicted as motions of points on the circumference or between the center and circumference of the unit circle. This approach will be used to depict the following rearrangements in six-vertex metal carbonyl cluster polyhedra: (1) Decarbonylation of the trigonal prismatic  $Co_6C(CO)_{15}^{2-}$  to the octahedral  $Co_6C(CO)_{13}^{2-}$ ; (2) Decarbonylation of either the pentagonal pyramidal or the  $C_2$  polyhedral  $(\mu_3-RP)(\mu_3-R'C)_2Fe_3(CO)_9$  to the  $C_3$  polyhedral  $(\mu_3-RP)(\mu_3-R'C)_2Fe_3(CO)_8$ ; (3) Reduction of bicapped tetrahedral  $Os_6(CO)_{18}$  to octahedral  $Os_6(CO)_{18}^{2-}$  through a topologically required  $C_{2v}$  six-vertex polyhedral intermediate.

## ANALOGY BETWEEN MIXED-METAL CLUSTERS

## AND MONONUCLEAR TRANSITION METAL PI-COMPLEXES

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To develop the Hoffmann's ideas about the isolobality of organic and organometallic fragments we discussed the next analogies:

1. 3e donor  $C_3H_5$  allyl ligand and  $RCo_2(CO)_6$  triangular fragment.
2. 4e donor  $C_4H_4$  cyclobutadiene ligand and  $Fe_2X_2(CO)_6$  fragment, where  $X = S, Se, Te$  and  $NPh$ .
3. 5e donor  $C_5H_5$  cyclopentadienyl ligand and binuclear fragments  $Cp_2Cr_2(SCMe_3)(S)_2$  or  $1/2 Cp_2Cr_2S_3$ .
4. 7e donor  $C_7H_7$  cycloheptatrienyl ligand and  $Cp_3MX_4$  cluster, where  $M = Cr$  or  $Mo$ ,  $X = O, S, NPh$ .

The choice of analogous fragment depends on similarity of geometry and spectral properties of mononuclear metal-containing fragment, for example  $Mn(CO)_3$ , when it bonds with organic ligand or cluster fragment respectively ("key-lock" principle). The original and literature data were used for the predict of the stability, structure, magnetic and redox properties of mixed-metal clusters, and the methods of their planned synthesis. In particular,  $Fe_2S_2(CO)_6$  was shown to be 2e, 4e or 6e donor ligand in its complexes with  $(PPh_3)_2Pt$ ,  $QRh$  or  $QFe$  fragments, respectively, where  $Q = Cp_2Cr_2(SCMe_3)(S)_2$ .

The chemistry of binuclear antiferromagnetic complex  $Cp_2Cr_2(OCMe_3)_2$  as a model of the active site of the ethylene polymerisation catalyst was shown to be analogous to vanadocene chemistry:



THERMAL DECOMPOSITION OF METAL ALKYLs OF V GROUP  
ELEMENTS IN THE GAS PHASE

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The kinetics of thermal decomposition of gaseous metal alkyls have been studied in a static system. The progress of the reaction was followed by measuring the amount of gaseous product formed.

It was established that the pyrolysis rate of these organometallics is a first order reaction. The rate constant was found to be markedly independent on the initial pressure and surface effects.

Temperature dependence on the rate constant ( $k$ ) for the process was calculated. The Arrhenius equations obtained by squares analysis are  $\ln k (s^{-1}) = 31,1 - 50400/RT$ ,  $\ln k (s^{-1}) = 27,7 - 41400/RT$  and  $\ln k (s^{-1}) = 25,5 - 29200/RT$  for  $Et_3As$ ,  $Et_3Sb$  and  $Et_3Bi$  respectively. These organometallics thermal stability decreases in the order  $As \rightarrow Sb \rightarrow Bi$ .

The obtained values of activation energies for pyrolysis triethylarsine, triethylstibine and triethylbismuth in fair agreement with  $\bar{D} [M - Et]$  derived from thermochemical data.

The thermal decomposition of arsine alkyls indicated that the pyrolysis rate is dependent upon the ligand nature and changes in the order  $Me < Et < n-Pr$ .

BOND DISSOCIATION ENERGIES AND THERMAL DECOMPOSITION  
SCHEMES OF d-METALS ALKYLAMIDES

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Seat of ways permitting to predict the direction of organometallic compounds thermal decomposition process still remains unsatisfaction. The present paper deals with the investigation of energies intramolecular distribution along  $M-NR_2$ ,  $N-R$  and  $M-M$  bonds as well as the study of d-metals alkylamides fragmentation and thermal decomposition processes. Reliabl values of heat combustion have been determined and standard formation heats of titanium tetradimethyl- and tetraethyldiamides have been calculated as a result of thermochemical investigations. Thermodynamic characteristics of the compounds vaporization process have been found and information about their vapor state have been obtained by static method. Using regular properties changes in related compounds series selected more correct thermodynamic characteristics for d-metals alkylamides have been chosen and on this basis thermodynamic values for alkylamides not studied yet have been reliabl estimatid by correlation method. Proceeding from intramolecular distribution of energies along bonds in diethyldiamides of metals considerable influence of coordination endoeffect in the  $N-C_2H_5$  has been substantiatid permitted to determine a more correct value of dissociation energy in dinuclear methyldiamides of molybdenum and tungsten as well as to substantiated  $N-C_2H_5$  dissociation energy necessary bonds dissociation energies calculation in d-metals ethyldiamides. The regularity established and metal-metal bond dissociation energy greater increase with respect to energy metal-alkylamides radical energy represent specific examples of bond changes analisis and may be regarded as a definite conception for a deeper development of which quontitative experimental data should be obtained. The thermal decomposition process schemes for methyl- and ethyldiamides of titanium, vanadium and chromium subgroups elements proposed on the basis of power values have definite conformation, based on literally and our experimental data, mass-spectrometry investigations and study of some mentioned metals alkylamides thermal decomposition.

## THE METAL PENTACARBONYL HALIDES ARE NOT ISOMORPHOUS

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The solution of metal pentacarbonyl halides  $M(CO)_5X$  [  $M = Mn, Re$ ;  $X = Cl, Br, I$  ] have very similar vibrational spectra in the carbon monoxide stretching region, but unexpectedly the crystalline state of the iodides behaved differently. The spectra of the iodides are remarkably simpler than those of the chlorides and bromides. They show no factor group splitting neither on  $B_1$  nor on  $A_1$  (axial) modes of the molecular  $\nu(CO)$ . also no transfer of Raman intensity between  $\nu(CO)$   $B_1$  and E modes was observed [1], a spectral behaviour that was observed on the chlorides and bromides. This spectral difference of the iodides surely lies in a difference of crystal structure from that of the other halides, which have a  $D_{2h}^{16}$  (Pnma) structure with  $Z = 4$ . Space group method was used to explain the iodides structure, a crystal structure of higher symmetry is suggested which perfectly in accord with their solid state spectra. The spectra also reveals that intermolecular vibrational interactions contribute more to dispersion than to factor group effects [2].

The suggested space group is also in accord with the fact that mixed crystal could be formed from  $Mn(CO)_5I$  and  $Mn(CO)_5Cl$ .

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DETAILED MECHANISM OF ETHYLENE HYDROGENATION  
BY  $\text{H}_4\text{Ir}(\text{PMe}_2\text{Ph})_3^+$ : DIHYDROGEN LIGAND AS A  
"GOOD LEAVING GROUP"

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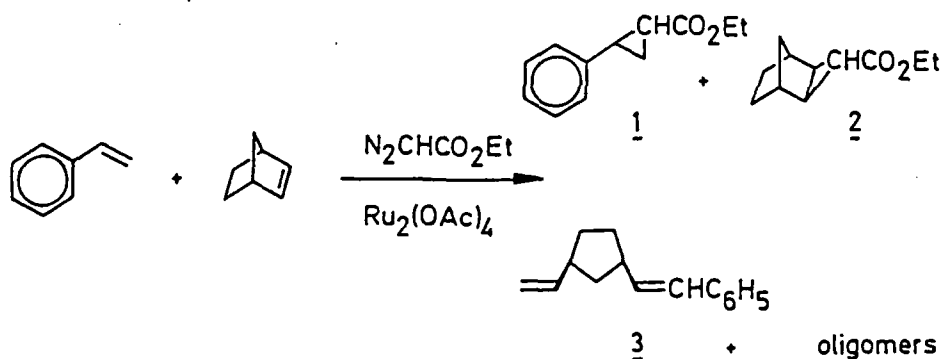
Protonation of a transition metal polyhydride furnishes a method for generating a catalytically-active reaction system. Thus, protonation of  $\text{H}_3\text{IrP}_3$  ( $\text{P} \equiv \text{PMe}_2\text{Ph}$ ) yields  $\text{H}_4\text{IrP}_3^+$  (an  $\text{H}_2$  complex), which reacts with ethylene to give  $\text{H}_2\text{Ir}(\text{C}_2\text{H}_4)\text{P}_3^+$ , which is then induced by additional ethylene to release ethane, with formation of  $\text{Ir}(\text{C}_2\text{H}_4)_2\text{P}_3^+$ . The *bis*-ethylene complex is unusual in being a stereochemically-rigid, trigonal bipyramid and having a high barrier to olefin rotation. This complex under  $\text{H}_2$ , liberates ethylene to give  $\text{H}_2\text{Ir}(\text{C}_2\text{H}_4)\text{P}_3^+$ , thereby closing a catalytic cycle. Further dynamic features of this complex, together with a description of its substrate selectivity, will be presented.

COMPETITIVE CYCLOPROPANATION AND CROSS-METATHESIS  
OF OLEFINS CATALYSED BY RUTHENIUM CARBOXYLATES

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It is well-established that rhodium(II) carboxylates are outstanding carbene-transfer catalysts (e.g., in cyclopropanation reaction)<sup>1</sup> whereas other binuclear tetracarboxylates are less efficient (Cu, Pd) or practically inactive (Cr, Mo, Fe, ...) for promoting typical carbene reactions. The recent report of the synthesis of diruthenium(II,II) acetate ( $\text{Ru}_2(\text{OAc})_4$ )<sup>2</sup> prompted us to test this complex in carbene chemistry. It appeared readily that rhodium and ruthenium-based systems promoted different reaction pathways. We report herein for the first time a clear-cut competition between catalytic reactions of cyclopropanation (carbene transfer) and metathesis of olefins. For instance, addition of ethyl diazoacetate to a mixture of styrene and norbornene containing a catalytic amount of  $\text{Ru}_2(\text{OAc})_4$  led both to cyclopropanes 1 and 2 and to products (3, selectively) resulting from a cross-metathesis of the olefins (Equation) <sup>3</sup>.



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CATALYTIC DECOMPOSITION OF HYDROGEN  
PEROXIDE WITH RESIN-TRANSITION METAL  
ION COMPLEXES CONTAINING AMINE AND  
AMMINE LIGANDS

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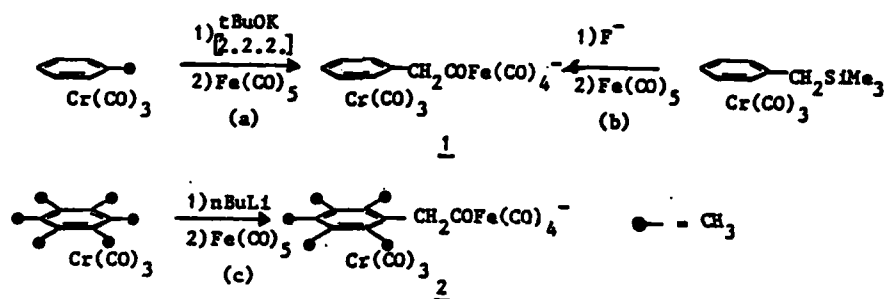
Dowex-50W resin (8% divinylbenzene crosslinking, 50-100 mesh) in the form of transition metal ion ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ) complexes containing the ligands  $\text{NH}_3$  and  $\text{C}_2\text{H}_5\text{NH}_2$  was used as potentially active catalyst in the  $\text{H}_2\text{O}_2$  decomposition. The structure of each complex in the resin was determined. The reaction was first order in all cases. The rate constant (per g of dry resin), the half time of the reaction and the molar distribution coefficient of the reactant were evaluated. The active species which was formed as an intermediate at the beginning of the reaction, had an inhibiting effect on the reaction rate. As a result of the  $\text{H}_2\text{O}_2$  decomposition, a coloured compound (peroxo-metal complex) was formed and was found to contain catalytic active species. Probable mechanisms for the reactions are proposed. The activation energy,  $E$  and the change in the entropy of activation,  $\Delta S$  with  $\text{C}_2\text{H}_5\text{NH}_2$ -complexes were greater than those with  $\text{NH}_3$ -complexes. The values of  $E$  and  $\Delta S$  with both ligands increased in the following sequence: Ni-complex ion < Co-complex ion < Cu-complex ion. This is the same sequence of the transition metal ionic size, taking into consideration that the  $\text{H}_2\text{O}_2$  decomposition by the copper-complex ion involves a redox reaction,  $\text{Cu(II)} \xrightarrow{+\text{e}^-} \text{Cu(I)}$ . The latter favours the catalytic decomposition of  $\text{H}_2\text{O}_2$ . The smaller the transition metal ion, the greater its electrical field, the more stable its complexes and the lower is the activation energy.

SYNTHESIS OF PHENYLACETYL ( $\eta^6$  CHROMIUM TRICARBONYL) TETRACARBONYL  
IRON ANIONS. APPLICATION TO THE  $\alpha,\alpha'$ -DIFUNCTIONNALIZATION OF  
HEXAMETHYLBENZENE

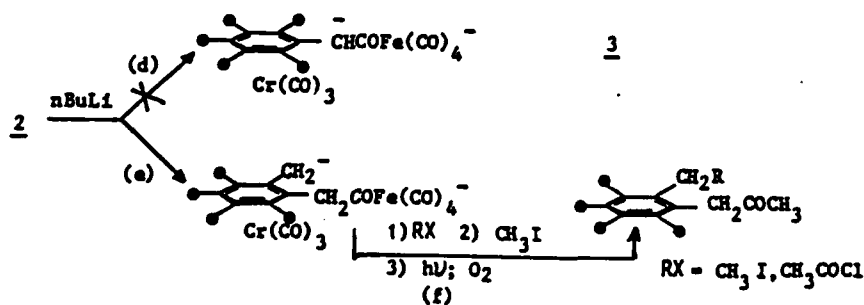
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Anions 1 and 2 were synthesized according to the following  
reaction schemes (a) or (b) and (c), and fully characterized by IR,  
 $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.



It was anticipated from the electrowithdrawing effect of the  $\text{Cr(CO)}_3$  moiety that, on reaction with  $\text{n Bu Li}$ , anion 2 could give dianion 3 (reaction d). In fact, deprotonation occurs on a methyl group in the ortho position, as shown by sequences (e) and (f).



These sequences open up a new entry into the  $\alpha,\alpha'$ -difunctionnalization of hexamethylbenzene.

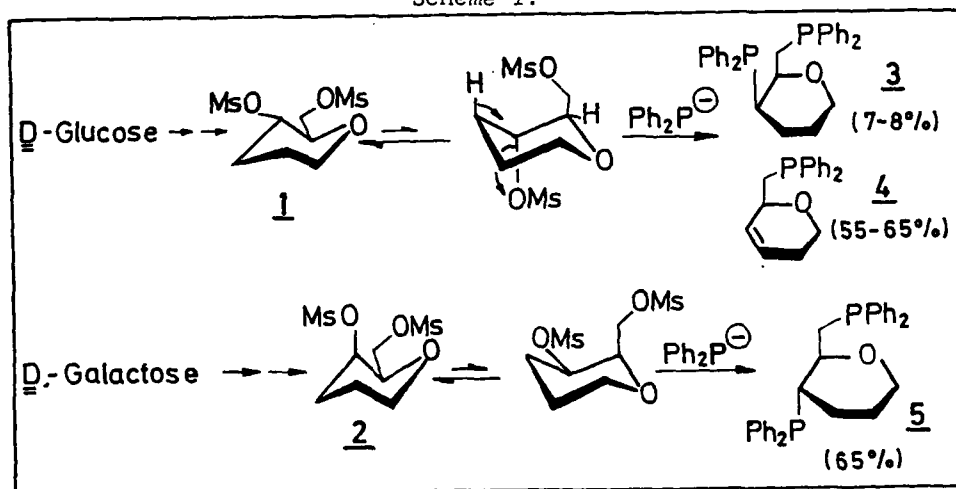
SYNTHESIS, CONFORMATIONAL PROPERTIES AND ENANTIOSELECTIVITY OF  
Rh(I) COMPLEXES OF DIPHOSPHINES DERIVED FROM D-GLUCOSE AND  
D-GALACTOSE

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Starting from D-glucose and D-galactose two dimesylates (1, 2) are prepared and converted into diphosphines 3 and 5 (Scheme 1.). Surprisingly, the reactivity of 1 and 2 towards diphenylphosphine anion, a sterically crowded nucleophile, was quite different; the main product from 1 was "anti - Saytzeff" elimination product 4. Conformational analysis, based on CD spectra of dibenzoate congeners of 1 and 2, explains these results.

Scheme 1.



Rh(I) complexes of 3 and 5, [Rh(NBD)(3)]ClO<sub>4</sub> (6) and [Rh(NBD)(5)]ClO<sub>4</sub> (7), exhibited interesting differences in CD and <sup>13</sup>C-NMR spectra. Direction of enantioselectivity of hydrogenation was the same with both catalytic complexes. Complex 7, being significantly more effective however, yielded over 90% e.e.s of chiral products on reduction of some unsaturated substrates.



# HOMOGENEOUS CATALYTIC CARBONYLATION OF STEROIDS WITH TRANSITION-METAL COMPLEXES

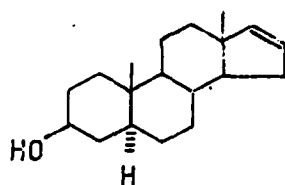
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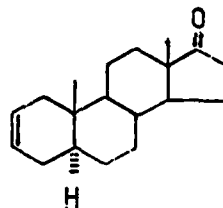
There is only few information<sup>1-2)</sup> in the literature about the catalytic carbonylation of steroids.

We investigated the carbonylation of several steroids with C=C double bonds in different positions (1,2,4,5,6,7,9/11/ and 16) with catalysts like  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Rh}_4(\text{CO})_{12} + \text{Et}_3\text{N}$ ,  $[\text{Rh}(\text{diene})\text{Cl}]_2 + \text{PR}_3$  (prepared in situ),  $\text{Pt}(\text{SnCl}_3)\text{Cl}(\text{PR}_3)_2$  and  $\text{PdCl}_2(\text{PPh}_3)_2$ .

$\Delta^{16}$ - (A) and  $\Delta^2$ -steroid (B) proved to be the most reactive.



(A)



(B)

In the hydroformylation with rhodium catalysts mainly the appropriate aldehydes have been formed (up to 70%), while addition of  $\text{Et}_3\text{N}$  favoured the formation of hydroxymethyl-derivatives (65%).

In the hydroalkoxycarbonylation of (A) regioselectivity (with the  $-\text{COOR}$  group in position 16) was 80%. The new compound was separated by column chromatography, purified by recrystallization and determined by GLC, MS and  $^{13}\text{C}$  NMR.

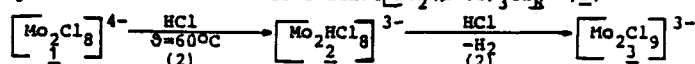
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# Homogeneous Catalytic Hydrogen Formation Using a Ditungsten Cluster and Low Valency Metal Ions in Aqueous Acidic Solutions

by  
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Multiply bonded dinuclear complexes of group VIB ( $M=Mo, W$ ) react with hydrogen halides e.g. proton oxidative addition to the  $[Mo_2Cl_8]^{4-}$ ,  $1$ , ion produces the hydride  $[Mo_2(\mu-H)(\mu-Cl)_3Cl_5]^{3-}$ ,  $2$ ; Diprotonation followed by loss of hydrogen gives the nonachloro derivative  $[Mo_2(\mu-Cl)_3Cl_5]^{3-}$ ,  $3$ ;



For the isoelectronic and isotuctural tungsten compound  $W_2Cl_8^{4-}$ ,  $4$ , reactions (1) and (2) occur<sup>3</sup> at  $-78^\circ C$  in  $HCl$  (12M) giving the corresponding  $[W_2(\mu-Cl)_3Cl_5]^{3-}$ ,  $5$ , ion, presumably via the reactive unstable hydride  $[W_2HCl_8]^{3-}$ ,  $5$ . Reactions (1) and (2) are easily reversible for molybdenum<sup>2,5</sup> but not for tungsten<sup>2,6</sup>. This enhanced susceptibility of W-W quadruple bonds towards protons and the irreversibility of these reactions has been the reason for a) the slow development of the chemistry of the  $W_2^{4+}$  unit and the long efforts for the isolation of  $4$  achieved eventually under non acidic conditions and b) the belief that these allegedly important catalytically species are in fact thermodynamic and kinetic sinks which makes them relatively uninteresting in terms of catalytic properties.

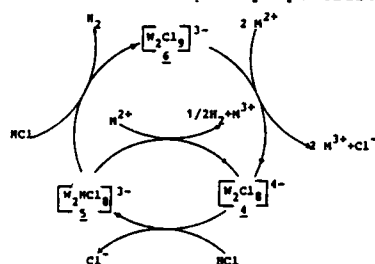


Fig. 1. The binuclear tungsten complex  $5$  catalyzes the evolution of  $H_2$  in  $HCl$  solutions with excess  $W_2^{2+}$  (aq),  $M=Cr, V$ .

We now report the facile two electron reductions of  $6$  by the chromous and vanadous chlorides to give  $4$  followed by decomposition and/or hydrolysis in aqueous solutions; In acid, decomposition is prevented by interception of reactions (1) and (2), thus  $6$  becomes an effective catalyst for the anaerobic oxidation of  $Cr(II)$  and  $V(II)$  to  $Cr(III)$  and  $V(III)$  with simultaneous hydrogen evolution as shown in Figure 1. Analogous results are obtained with  $3$  but because the rates of reactions (1) and (2) are relatively slow the cycle can be monitored by electronic spectroscopy and the intermediate products can be isolated. The system although not directly related to hydrogen producing systems (water splitting or homogeneous catalysts for the water gas-shift reaction)<sup>7,8</sup> it is nevertheless relevant and of great interest.

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## DISPLACEMENT OF AN AQUO GROUP BY OLEFINS IN SOME WATER

## SOLUBLE RUTHENIUM(III) COMPLEXES

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Ruthenium complexes have been found to be efficient catalysts for various reactions such as oxidation, hydrogenation and carbonylation of olefins [1-3]. The synthesis of mixed ligand organometallic complexes of olefins can give a lead in understanding the mechanism of such reactions.

The present investigation deals with the synthesis and characterization of some water soluble mixed ligand organometallic complexes of Ru(III) involving mono and di-olefins such as cyclohexene, cyclooctene and 1,5 cyclooctadiene. Mixed ligand complexes of the composition  $K_2[RuCl_5L]$  (where  $L$  = cyclohexene, cyclooctene) and  $[RuCl_3(cyclooctadiene)]_2$  were synthesized by the interaction of  $K_2[RuCl_5(H_2O)]$  and the corresponding olefin in a 1:1 mole ratio in  $H_2O$ -EtOH mixture. The complex  $[Ru(EDTA-H)(cyclohexene)]$  was synthesized by the displacement of  $H_2O$  from the coordination sphere of  $[Ru(EDTA-H)(H_2O)] \cdot 2H_2O$  by cyclohexene.

The above mentioned complexes were characterized by elemental analysis, conductivity measurements, IR, UV-vis and NMR spectroscopy. All the olefin complexes are water soluble except for the cyclooctadiene dimer.

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**Silica Supported Ruthenium and Osmium Carbonyls as Catalysts for Cycloocta-1,5-diene Isomerization.**

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Homogeneous and heterogenized ruthenium and osmium catalysts derived from  $M_3(CO)_{12}$  ( $M = Ru, Os$ ) are used in the isomerization of cycloocta-1,5-diene (1.5 cod) to the 1.4 and 1.3 isomers. Their activities and selectivities in 1.4 isomer -which has recently been reported as an interesting starting material for a polymerization reaction- [1] are compared both in flow and in batch conditions, operating in the range of temperature 40-125°C. Selectivities up to 90% and yields as high as 50% in 1.4 cod have been obtained. Interestingly, surface organometallic ruthenium species show a higher catalytic activity than the homogeneous one, which deactivates during the reaction due to formation of a mixture of tri- and tetranuclear Ru clusters with coordinated 1.5 cod [2]. By air oxidation of the  $Ru_3(CO)_{12}/SiO_2$  species a mononuclear surface carbonyl is obtained [3] which maintains a good catalytic activity and can be recycled without significant loss of catalytic activity. The nature and the stability of the heterogenized catalyst have been investigated by i.r. spectroscopy.

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NIOBIUM(V) CHLORIDE AS HOMOGENEOUS CATALYST FOR THE TRIMERIZATION  
OF ALKYNES

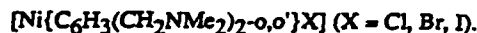
J.A.K. du Plessis, C.J. du Toit and G. Lachmann, Department of  
Chemistry, Potchefstroom University for C.H.E., Potchefstroom  
2520, Republic of South Africa

Niobium(V) chloride trimerizes phenylacetylene to 1,2,4- and 1,3,5-triphenylbenzene, 1,7-octadiyne to 1,4-bis-(6-tetralin)-butane and 1-hexyne to 1,2,4- and 1,3,5-tributylbenzene.

The course of the reactions is characterized by three phases. In the first phase 2 moles of the mono-alkynes or one mole of the dialkyne per mole niobium is rapidly absorbed to give a niobium(V) complex. This is followed by an induction period during which the active trimerization catalyst is formed by a spontaneous reduction of the niobium(V) to a niobium(III) complex.<sup>1</sup> In the third phase the alkynes are converted to the trimers. If a mixture of phenylacetylene and 1,7-octadiyne is used the expected trimers as well as a co-trimer, 6-phenyl-tetralin are formed. With phenylacetylene and 1-hexyne the co-trimers phenyldibutylbenzene and diphenylbutylbenzene are formed. In all these cases phenylacetylene played the most important role during the activation of the catalytic system.

<sup>1</sup> G. Lachmann, J.A.K. du Plessis and C.J. du Toit, J. Mol. Catal., 1987, 42, 151.

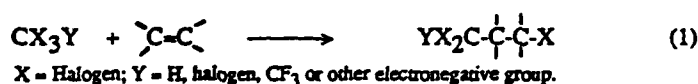
NEW HOMOGENEOUS CATALYSTS IN THE ADDITION  
OF POLYHALOGENOALKANES TO OLEFINS; ORGANONICKEL(II) COMPLEXES



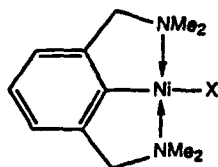
David M. Grove, Gerard van Koten, and Augustinus H. M. Verschuuren,

Department of Metal-Mediated Synthesis, Laboratory of Organic Chemistry, Transitorium III,  
University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands.

The Karasch addition of polyhalogenoalkanes to an alkene double bond, eq 1, is amenable to catalysis by various metal complexes.



We now report that the square planar Ni(II) organometallics **1a-c** [1], Fig. 1, are very active homogeneous catalysts for the Karasch addition under very mild conditions. Some quantitative results for the **1a** catalysed addition of the perhaloalkanes  $\text{CCl}_4$ ,  $\text{CBr}_4$ , and  $\text{CF}_3\text{CCl}_3$  to the terminal alkenes hept-1-ene, and methyl methacrylate are presented. For example, the addition of



$\text{X} = \text{Cl, 1a}$

$\text{X} = \text{Br, 1b}$

$\text{X} = \text{I, 1c}$

Figure 1

$\text{CCl}_4$  to methyl methacrylate in  $\text{CH}_3\text{CN}$  catalysed by < 0.1 mole % of **1a** (relative to alkene) affords the 1:1 adduct  $\text{CCl}_3\text{CH}_2\text{CCl}(\text{Me})\text{CO}_2\text{Me}$  in high yield with 100 % regioselectivity. Kinetic experiments at 30 °C show turnover numbers of more than  $500 \text{ h}^{-1}$  for the first hour of the reaction. This catalytic behaviour is clearly related to the fact that **1a-c** are easily oxidized to novel air-stable nickel(III) species  $[\text{Ni}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}o,o'\}\text{X}_2]$  [2].

The fairly rigid *N,C,N* chelation of the ligand in and the consequent restrictions imposed on the catalytic site(s) makes these species well suited for mechanistic investigations.

References:

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INFLUENCE OF THE NATURE OF THE ORGANOMETALLIC COMPONENT  
ON THE CATALYTIC ACTIVITY AND PRODUCT SELECTIVITY IN  
METATHESIS REACTION

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A comparative study of the effect of the nature of the organometallic compound on the catalytic activity and product selectivity in metathesis reaction of unsaturated alicyclic esters (e.g. methyl and ethyl cyclohexylidene and cyclopentylidene acetates) in the presence of  $WCl_6$ -based catalysts was performed. When using organotin (e.g.  $Me_4Sn$ ,  $Bu_4Sn$ ,  $Ph_4Sn$ ) and organoaluminium compounds (e.g.  $Et_2AlCl$ ,  $EtAlCl_2$ ) in the catalytic system the following results were obtained:

- (i) organotin compounds were more selective for metathesis products than organoaluminium compounds;
- (ii) the selectivity in metathesis products varies in the order:  $Me_4Sn > Ph_4Sn > Bu_4Sn$ ;
- (iii) the catalytic activity induced by the organoaluminium compounds is high but the selectivity in metathesis products remains low;
- (iv) the catalytic systems with organoaluminium compounds lead preferentially to isomerization and oligomerization reactions.

These results are attributed to a distinct alkylating and reducing power of the organometallic compound used in the catalytic system, the generation of metallacarbenes of different types and reactivities through the interaction of the organometallic compound with  $WCl_6$  and differences in the Lewis type acidity of the organometallic compound employed. The mode of interaction of the above organometallic compounds with  $WCl_6$  and the ways of generation of the intermediate metallacarbene species are discussed in detail.

ORGANO-PALLADIUM COMPOUNDS IN CATALYSIS OF DIAZO  
ALKANES DECOMPOSITION

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Catalyzed by  $\text{Pd}(\text{OAc})_2$  in benzene solutions at  $35^\circ\text{C}$  decomposition of diphenyl diazo methane has been shown to proceed with  $\text{N}_2$  elimination and benzophenone azine (I) formation. In addition to (I) palladium complex  $\text{Pd}_4(\eta\text{-OAc})_4[\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{N}=\text{N}=\text{C}(\text{Ph})\text{C}_6\text{H}_4]_2$  (II) containing ortho-palladated azine ligands has been isolated and characterised by analytical, spectral (IR, NMR) and molecular mass data. The thermolysis of (II) in  $\text{AcOH}/\text{C}_6\text{H}_6$  solutions at  $50\text{--}60^\circ\text{C}$  yields trinuclear palladium complex  $\text{Pd}_3(\eta\text{-OAc})_4[\text{C}_6\text{H}_4\text{C}(\text{Ph})=\text{N}=\text{N}=\text{C}(\text{Ph})\text{C}_6\text{H}_4]$  (III) also containing ortho-palladated azine ligand. According to single crystal X-ray structure determinations of (III) Pd atoms are shaped like a bent metal chain with Pd-Pd-Pd angle of  $73.1^\circ$  and Pd-Pd distances of  $3.102 - 3.157 \text{ \AA}$ . The neighboring Pd-atoms are bridges by the pairs of AcO-groups, and the terminal Pd-atoms of the chain are coordinated by N-atom and ortho-C-atom of the azine ligand.

Under reaction conditions ( $\text{C}_6\text{H}_6$ ,  $35^\circ\text{C}$ )  $\text{Pd}(\text{OAc})_2$  and (I) does not form complex (II), suggesting the complex (II) to be formed through carbene intermediates.



## FACILE HYDRIDE MIGRATIONS IN MODEL BINUCLEAR CATALYSTS

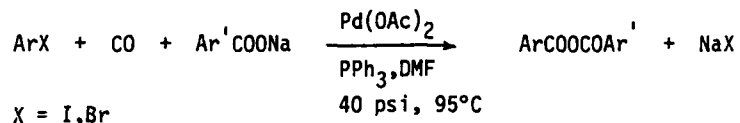
Martin Cowie and Brian A. Vaartstra, Department of Chemistry,  
University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

The complexes,  $[MM'(CO)_2(\mu-X)(DPM)_2]^{n+}$  ( $M, M' = Rh, Ir$ ;  $X = Cl, I$  ( $n = 1$ );  $X = S$  ( $n = 0$ );  $DPM = Ph_2PCH_2PPh_2$ ), have been studied as models of the binuclear hydrogenation catalyst,  $[Rh_2(CO)_2(\mu-Cl)(DPM)_2]^+$ . All model complexes react readily with  $H_2$  to give a range of dihydride species which in some cases react further to yield tetrahydrides. NMR studies ( $^1H$ ,  $^1H\{^{31}P\}$  and  $^{31}P\{^1H\}$ ) on these species have yielded valuable information on the facile hydride migrations occurring. In all cases oxidative addition of  $H_2$  appears to take place at one metal centre in the A-frame "pocket" between the metals. However in the chloride- and sulfide-bridged diiridium complexes the hydride ligands rearrange to positions, one on each metal, on the "outside" of the complexes. The mechanism for these rearrangements will be discussed. Subsequent reactions of the dihydride complexes with alkynes have helped elucidate the ways in which binuclear hydrides may interact with unsaturated substrate molecules and the relationship of this chemistry to binuclear hydrogenation catalysis will be discussed. The involvement of the adjacent metal centres in this chemistry will be emphasized.

ANHYDRIDE SYNTHESIS BY HOMOGENEOUS PALLADIUM(II)  
CATALYZED CARBONYLATION REACTIONS OF ARYL HALIDES

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There has been considerable interest in metal complex catalyzed routes to acid anhydrides. However, in general, product yields are low and stringent conditions are required. It has now been found that aryl halides react with



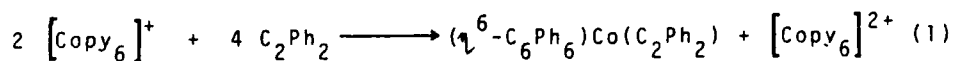
carbon monoxide and sodium or calcium carboxylate in N,N-dimethylformamide, in the presence of catalytic quantities of palladium acetate, to give anhydrides in reasonable yields. The influence of different factors (solvent, substituent effects), as well as a proposed reaction mechanism, will be discussed.

The  $[\text{Copy}_6][\text{BPh}_4]$  - Promoted Cyclotrimerization and Hydrodimerization of Alkynes

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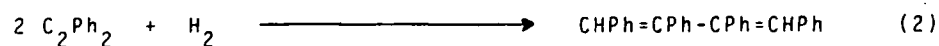
Pier Francesco Zanazzi, Dipartimento di Scienze della Terra, Università di Perugia, I-06100, Italy.

Pyridine solutions of the cationic  $\text{Co(I)}$  complex  $[\text{Copy}_6][\text{BPh}_4]^+$  promote the cyclotrimerization of both terminal and internal alkynes at room temperature. However diphenylacetylene behaves differently, and induces the disproportionation of  $\text{Co(I)}$  to  $\text{Co(0)}$  and  $\text{Co(II)}$  (eq 1).



The molecular structure of  $(\eta^6\text{-C}_6\text{Ph}_6)\text{Co}(\text{C}_2\text{Ph}_2)$  has been solved by X-ray diffraction methods and the compound constitutes the first example of a long-lived radical, half-sandwich mononuclear cobalt complex.

The slow addition of alkynes to  $[\text{Copy}_6][\text{BPh}_4]$  in pyridine solution under a hydrogen atmosphere, brings about gas absorption and butadienes are formed according to equation 2.



The reaction constitutes the first example of alkyne hydrodimerization which occurs catalitically and employing dihydrogen instead of metal hydrides<sup>2</sup> or aluminium alkyls<sup>3</sup>. Polypyridines inhibit the above mentioned reactions.

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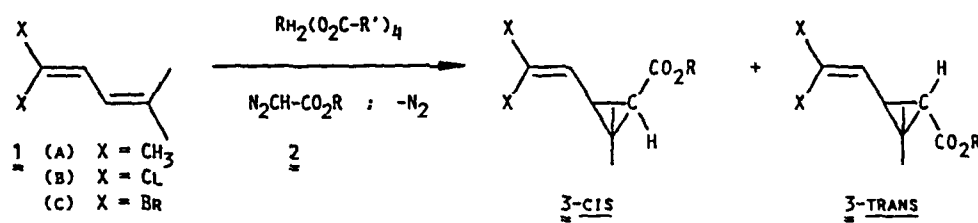
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CATALYTIC CYCLOPROPANATION OF DIENES :  
STERESELECTIVE SYNTHESIS OF PYRETHROIDS FROM DIAZOACETATES  
AND 1,1-DISUBSTITUTED-4-METHYLPENTA-1,3-DIENES

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Pyrethroids derived from chrysanthemic acid 3.A (R=H), permethric acid 3.B (R=H) and deltamethric acid 3.C (R=H), exhibit exceptionally potent insecticidal activity together with very low mammalian toxicity and rapid biodegradability. These remarkable properties are at the basis of intense effort to devise syntheses suitable for the industrial production of pyrethroids.

We have already described the cyclopropanation of olefins and dienes catalysed by rhodium acetate <sup>1</sup>.



We now report that the use of rhodium(II) carboxylate catalysts for the addition of diazoacetates 2 to dienes 1 affords cyclopropanecarboxylates 3 containing substantially more of the insecticidally preferable cis-isomer which has the substituted vinyl and alkoxy carbonyl groups on the same side of the cyclopropane ring, than is obtained using other catalysts, namely the better known copper catalysts <sup>2,3</sup>. The cyclopropanecarboxylates 3 are then readily converted into pyrethroids insecticides.

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IRON-PROMOTED REGIO-, STEREO- AND ENANTIOSELECTIVE ADDITION OF  
ALKENES TO 1,3-DIENES AND NORBORNADIENE

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The complexes of the type  $(DAD)FeX_2$  ( $DAD = \text{diazadiene } RN=CR'-CR'=NR$  or similar pyridylimines) are easily converted to catalytically active species " $(DAD)Fe$ " by reaction with butadiene-magnesium. In the presence of 1,3-dienes a smooth catalytic reaction to cyclodimers occurs at ambient temperature [1]. In the presence of terminal olefins the simple isodimerization is suppressed and an addition of the olefin to the diene is favoured instead. The terminal olefin may carry n-alkyl, iso-alkyl or aromatic substituents. The scope of the reaction has been expanded to many mono- and disubstituted dienes as well. As a function of steric requirements of the DAD the stereochemistry of the products can be controlled (linear or branched addition products); chiral DADs, like in the isodimerization reaction [1], give considerable enantiomeric excess, e.g. in the formation of 3-methyl-1,2,4-hexadiene from ethene and piperylene. A similar chiral iron-organic catalyst induces the asymmetric coupling of ethene and norbornadiene to 3-vinyl-tricyclo[2.2.1.0<sup>2,6</sup>]-heptane [2].

Isolated  $(DAD)Fe(\text{norbornadiene})(L)$  complexes afford details to understand the stereochemical course of these catalytic reactions as well as the catalytic coupling of norbornadiene with alkynes or 1,3-dienes [3].

[1] H. tom Dieck, J. Dietrich, *Angew. Chem. Int. Ed. Engl.* 24 (1985) 791.

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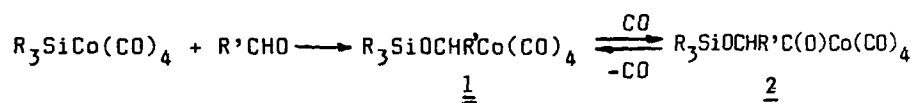
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MODELS FOR CO REDUCTION. PREPARATION OF DINUCLEAR COBALT  
CARBONYLS WITH THE CARBENE MOIETY  $C(OSiR_3)CH_2OSiR_3$

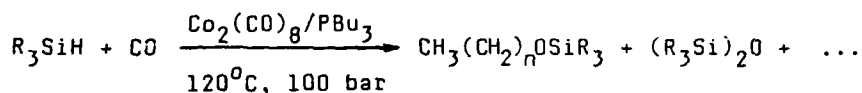
Attila Sisak, Márta Máté, László Németh

Institute of Organic Chemistry, University of Veszprém,  
Schönherz Z.u.10., H-8200, Veszprém

The complexes  $R_3SiCo(CO)_4$  ( $R = Me, Et, Ph$ ) react with aliphatic aldehydes to give  $\alpha$ -silyloxymethyl- and  $\alpha$ -silyloxyacetylcobalt tetracarbonyls<sup>1,2</sup>:



1 and 2 are stable only in the case of  $R'=H$ . The reaction with gaseous formaldehyde could be promoted by catalytic amounts of bases (e.g.  $PBu_3$ ) and/or UV irradiation. Depending on the relative concentration of the base and other reaction conditions 1, 2, or  $Co_2(CO)_7$  ( $\mu-C(OSiR_3)CH_2OSiR_3$ ) (3) were found, respectively as main products. The complexes are characterised by their IR, NMR and mass spectra and elementary analysis. We observed the complexes 3 also in the reaction mixtures of the catalytic hydrosilylation of CO in the presence of  $Co_2(CO)_8$  and bases<sup>3</sup>:



$R_3 = Et_3, MeEt_2$ ;  $n = 0-5$

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3. Sisak, A.; Angyalosy, Z.: unpublished results.

# REACTIVITY OF METALLIC COPPER WITH ORGANIC COMPOUNDS IN THE PRESENCE OF MOLECULAR OXYGEN.

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The role of Cu(I) and Cu(II) in promoting oxygen activation both in chemical and biological systems has been widely discussed <sup>1,2</sup>. However, little is known about the interaction of metallic copper with molecular oxygen<sup>3</sup>.

We have already studied the reaction of metallic Cu with CH<sub>3</sub>OH and PhOH in the presence of oxygen and pyridine to give Cu(OCH<sub>3</sub>)<sub>2</sub> and 4,5-dimethoxy-1,2-benzoquinone<sup>4</sup>.

The observation that the more acidic phenol (pK<sub>a</sub>=9.89) reacts much more smoothly than the less acidic methanol (pK<sub>a</sub>=16) and the necessity to operate in the presence of a coordinating base suggest that the activation and complexation of the organic reagent requires a hydrogen abstraction as a preliminary step.

To prove this hypothesis we have reacted very weak acids, such as ethanol and phenylacetylene, with O<sub>2</sub> which caused very slow oxygen consumption, whereas organic molecules lacking mobile hydrogen atoms failed to react.

This point of view is confirmed also by the very easy interaction of Cu and O<sub>2</sub> with benzoic acid (pK<sub>a</sub>=4.19) and CH<sub>3</sub>NO<sub>2</sub> (pK<sub>a</sub>=10.2). The latter reaction is particularly interesting as it gives cyanide, isocyanate and nitrito compounds depending on the reaction conditions.

The recent application of analytical surface techniques which allow the detection of peroxo species and adsorbed atomic oxygen on Cu, and the results reported by Rao et al.<sup>5</sup> on the interaction of polycrystalline Cu surface with molecular oxygen and proton donor molecules agree with our hypothesis on the role played by the base in promoting hydrogen abstraction.<sup>1</sup>

<sup>1</sup> Houben-Weyl, "Methoden der Organische Chemie", IV/1b, Georg Thieme Verlag, p. 55-67 (1976)

<sup>2</sup> K.D.Karlin and J.Zubieta (eds.), "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives", Adenine Press, Guilderland, N.Y., (1983)

<sup>3</sup> K.Prabhakaran, P.Sen and C.N.R. Rao, Surface Sci., **177**, L971 (1986)

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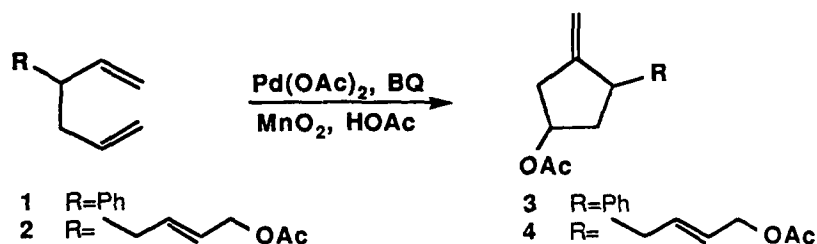
<sup>5</sup> K.Prabhakaran, P.Sen and C.N.R. Rao, Surface Sci., **169**, L301 (1986)

# PALLADIUM-CATALYZED OXIDATIVE CYCLIZATION OF 1,5-DIENES

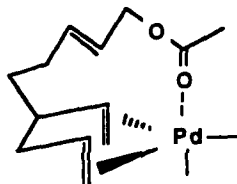
Thomas Antonsson<sup>a</sup>, Christina Moberg<sup>a</sup>, Louise Totté<sup>a</sup>, and Andreas Heumann<sup>b</sup>

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Previously, we have reported that substituted 1,5-dienes, e.g. 1 and 2, undergo oxidative ring-closure catalyzed by palladium acetate using p-benzoquinone and MnO<sub>2</sub> as oxidants to give functionalized cyclopentanes. The reaction shows a high degree of regioselectivity affording mainly 3 and 4.



The stereoselectivity of the cyclizations differs, however. The product obtained from cyclization of the allylic acetate 2 gives a trans/cis ratio of about 2/1 whereas the product obtained from the diene 1 gives a trans/cis ratio of 1/1. A possible explanation for this difference may be a weak coordination of the acetate group to palladium which would favour a pseudo-equatorial palladium-diene complex thereby increasing the trans-adduct formation.



In order to investigate whether increased stereoselectivity results from coordination of a functional group to palladium, a series of 3-O-substituted 1,5-dienes carrying alcohol, nitrile, acetate and carboxylic acid groups at various distances from the diene center were prepared and allowed to undergo the cyclization reaction.

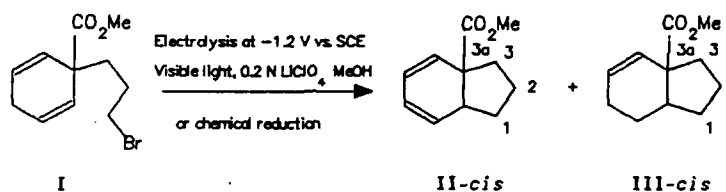


**CARBON-CARBON BOND FORMATION CATALYZED BY VITAMIN B<sub>12</sub>  
STEREOCHEMISTRY AND MECHANISM**

Heng Su, Eugen Eichenberger, Rolf Scheffold.

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Freiestr. 3, CH-3012 Bern, Switzerland

Vitamin B<sub>12</sub> acts as a catalyst in reductive, intra- and intermolecular, radical-type C,C-bond formation [1]. Reductive cyclisation of achiral bromodiene I affords chiral *cis*-diene II and chiral *cis*-monoene III. The ratio by which the two products II and III are formed as well as the enantiomeric excesses in II and III strongly depend on the reaction conditions.



Catalyst or reagent	Total	Products Ratio	
Reaction condition	Yield, %	[% e. e. of major enantiomer]	
B <sub>12</sub> (5 mol%) Pt-Cathode	92	98 [<1%, 3a(S)]	<2
B <sub>12</sub> (5 mol%) C-Cathode	73	50 [14%, 3a(S)]	50 [12%, 3a(R)]
B <sub>12</sub> (5 mol%) Zn/NH <sub>4</sub> Cl/DMF	74	7	93
Bu <sub>3</sub> SnH C <sub>6</sub> H <sub>6</sub> /reflux	98	<2	98 [2]

The mechanism and the stereochemistry of the B<sub>12</sub>-catalyzed C,C-bond formation will be discussed.

[1] R. Scheffold, M. Dike, Th. Herold and L. Walder, *J. Am. Chem. Soc.* 1980, 102, 3642.

[2] A. L. J. Beckwith and D. H. Roberts, *J. Am. Chem. Soc.* 1986, 108, 5893.

VITAMIN B<sub>12</sub>-CATALYZED TANDEM RADICAL CYCLIZATION

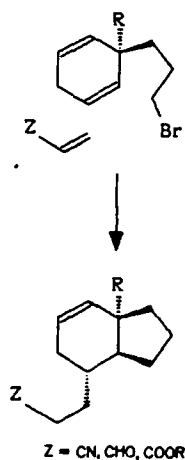
E. Eichenberger, R. Härter, H. Su, R. Scheffold

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Freiestr. 3, CH-3012 Bern, Switzerland

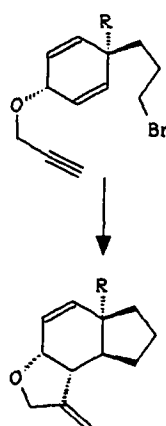
The vitamin B<sub>12</sub>-catalyzed chemical or electrochemical reduction of alkylhalides in presence of a suitable chosen set of two or more intra- or intermolecularly located C,C- multiple bonds offers a flexible strategy for the stereoselective formation of two or more C,C- bonds in one operation (Tandem Reaction)<sup>[1,2]</sup>.

Three of four combinations of intra- and intermolecular formation of two C,C- bonds are of relevance in synthesis. Examples for each type, intra - inter, intra - intra and inter - intra are presented.

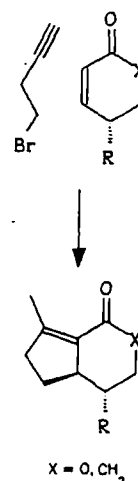
Intra - Inter  
Cyclization with  
chain extension



Intra - Intra  
Double cyclization



Inter - Intra  
Annellation



Synthesis of natural products based on B<sub>12</sub>-Tandem cyclization will be presented.

[1] R. Scheffold, *Nachr. Chem. Tech. Lab.* 1988, 36, 261.

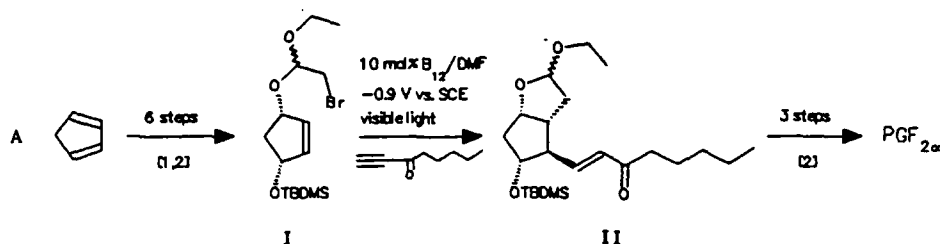
[2] Ch. Weymuth, *Euchem Conf.* "Semiocchemicals in the Plant and Animal Kingdom", Angers 12.-16. Oct. 1987.

PROSTAGLANDIN SYNTHESIS *via* VITAMIN B<sub>12</sub>-CATALYZED  
C-C-BOND FORMATION

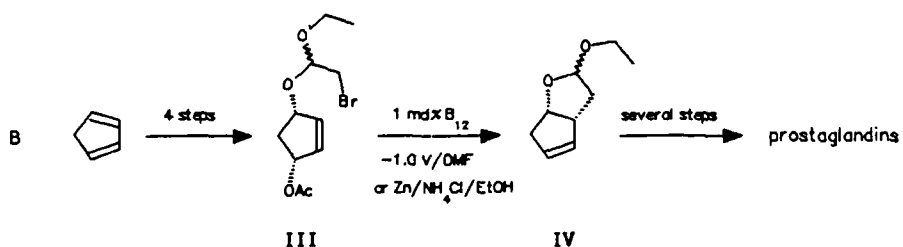
S. Busato, O. Tinembart, R. Scheffold

Department of Organic Chemistry, University of Bern,  
Freiestr.3, CH-3012 Bern, Switzerland

The key reaction in a short synthesis of (+)-prostaglandin F<sub>2α</sub> is the vitamin B<sub>12</sub>-catalyzed electrolysis of the bromoacetal I in the presence of 1-octyn-3-one, affording directly II in good yield.



The bromoacetal III on B<sub>12</sub>-catalyzed reduction affords the olefin IV in high yield.



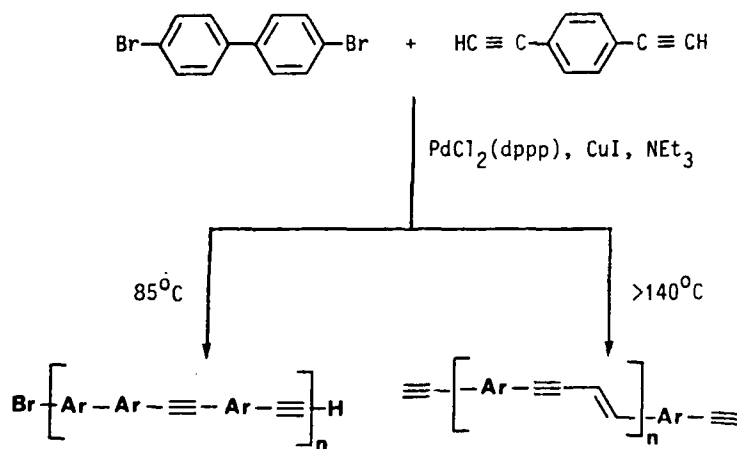
B<sub>12</sub> acts as a mediator in the electron-transfer<sup>[3]</sup> from the electron source to the bromides I or III, creating a radical which undergoes cyclization. The cyclized radical intermediate adds to the Michael-system (reaction A) or undergoes elimination (reaction B).

- [1] K. Laumen, M.P. Schneider, *J.Chem.Soc.,Chem.Comm.* 1986, 1298.
- [2] G. Stork, P.M. Sher, H.L. Chen, *J.Am.Chem.Soc.* 1986, 108, 6384.
- [3] R. Scheffold, S. Abrecht, R. Orlinski, H.-R. Ruf, P. Stamouli, O. Tinembart, L. Walder, C. Weymuth, *Pure & Appl.Chem.* 1987, 59, 363.

TEMPERATURE DEPENDENT REACTION PATHWAYS IN PALLADIUM-  
CATALYSED C-C BOND FORMATIONS

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University of East Anglia, Norwich NR4 7TJ, U.K.

Aromatic polymers are chemically inert, extremely tough and very resistant to heat. They have therefore found widespread use in engineering applications. The C-C cross-coupling reaction of dihaloarenes with dialkynylarenes in the presence of palladium catalysts gives access to a new range of these materials. The structure of polymers obtained under two different temperature regimes suggests that two reaction pathways are followed, and that at higher temperature alkyne polymerisation dominates over cross-coupling:



The polymers are characterised by FTIR, FT-Raman, DSC and solid-state  $^{13}\text{C}$ -MAS NMR.

VALENCE CHANGES OF ORGANIC COMPLEXES OF CHROMIUM AND  
VANADIUM IN CATALYTIC HYDROPEROXIDE ALKANE OXIDATION

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G.A. Razuvaev, Chemistry Institute of the USSR Academy of  
Sciences, Gorky, USSR

Hydroperoxide alkane oxidation catalyzed by organic chromium and vanadium complexes has been investigated in the detail in the present work. Under this conditions  $C_5-C_{15}$  alkanes are oxidized to alkanones with good selectivity at temperatures 60 to 110°C, i.e. under more mild conditions than on autooxidation. Chromium(III)- and vanadium(IV)-acetylacetonates and alcohols and in addition carboxylates, derivatives of polyatomic alcohols, carbonyls for chromium (III, O) are studied as catalysts. Hydroperoxide oxidation does not demonstrate features characteristic of chain radical processes. The first stage of the process is a rapid formation of different stoichiometry equilibrium complexes of the initial organometallic compound with tert-butyl hydroperoxide. Intracomplex oxidation of initial metal atom to higher oxidation state proceeds in the complex which limits the rate of hydroperoxide alkane oxidation. Alkylperoxochromate(VI) or alkylperoxovanadate(V) formed oxidized alkane. The simultaneous attack of methylene group of alkane by peroxide and chromate (vanadate) groups occurs in alkylperoxochromate (VI)- or alkylperoxovanadate (V)-alkane complex and this determines the selective formation alkanones. Such alkylperoxovanadate has been synthesized in case of vanadium; its ability to alkane oxidation has been indicated.

Reactivity of the unsaturated carbonyl  $[\text{Mn}_2\text{H}_2(\text{CO})_6(\text{dppm})]$   
towards small molecules

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Italy.

Recently the carbonyl complex  $[\text{Mn}_2\text{H}_2(\text{CO})_6(\text{dppm})]$ , **1**, containing the unsaturated fragment  $(\mu\text{-H})_2\text{Mn}_2(\text{Mn}=\text{Mn})$ , has been synthesized in our laboratory. We report now some results on the reactivity of **1** towards small molecules under mild conditions.

Compound **1** shows patterns of reactivity not observed previously in related unsaturated hydrido-carbonyl complexes. Thus **1** reacts with RCN, (R=Me, Et) to give  $[\text{Mn}_2(\mu\text{-}\sigma, \pi\text{-NCR})(\text{CO})_6(\text{dppm})]$ , rare examples of complexes with  $\pi$ -bonded nitriles, but the expected<sup>(1)</sup>  $[\text{Mn}_2(\mu\text{-H})(\mu\text{-N=CHR})(\text{CO})_6(\text{dppm})]$  are obtained for R=Ph, HC=CH<sub>2</sub>. The reaction of **1** with *t*-BuNC yields  $[\text{Mn}_2(\mu\text{-}\sigma, \pi\text{-CN-}t\text{-Bu})(\text{CO})_6(\text{dppm})]$  in contrast with the behaviour of  $[\text{Re}_2\text{H}_2(\text{CO})_6(\text{dppm})]$ <sup>(1)</sup> or  $[\text{Mn}_2\text{H}_2(\text{CO})_4(\text{dppm})_2]$ <sup>(2)</sup>. On the other hand, **1** reacts with RCOOH to afford  $[\text{Mn}_2(\mu\text{-H})(\mu\text{-OOCR})(\text{CO})_6(\text{dppm})]$  while CF<sub>3</sub>COOH adds oxidatively to Os<sub>3</sub>H<sub>2</sub>(CO)<sub>10</sub><sup>(3)</sup>. Complex **1** also reacts with aldehydes to give  $[\text{Mn}_2(\mu\text{-H})(\mu\text{-OR})(\text{CO})_6(\text{dppm})]$ .

- (1).- D.W. Prest, M.J. Mays, P.R. Raithby. J.Chem. Soc., Dalton Trans., 1982, 2021.
- (2).- H.C. Aspinall, A.J. Deeming. J. Chem. Soc., Chem. Commun., 1983, 839.
- (3).- E.D. Korniets, L.K. Kedrova, N.I. Pavlenko. Izv. Akad. Nauk. SSSR, Ser. Khim. 1986, 2310.

Reactions of  $[\text{Mn}_2\text{H}_2(\text{CO})_6(\text{dppm})]$  and  $[\text{Mn}_2(\text{CO})_8(\text{dppm})]$  with terminal alkynes.

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A. Tiripicchio, M. Tiripicchio-Camellini. Istituto di Chimica Generale ed Inorganica. Università di Parma. 23100 Parma. Italy.

It is well known that acetylenes are among the simplest and most reactive organic molecules, therefore they have been used as ideal starting materials for many different purposes. We report here the early results on the reactivity of terminal alkynes with carbonyl complexes  $[\text{MnH}_2(\text{CO})_6(\text{dppm})]$ , 1, and  $[\text{Mn}_2(\text{CO})_8(\text{dppm})]$ , 2, at r.t. or under U.V. irradiation ( $-10^\circ\text{C}$ ) respectively.

Since  $\text{H}_2$  loss from 1 or CO evolution from 2 would yield seemingly the same intermediates, it could be anticipated that some common products might be obtained in the reactions of acetylenes with either 1 or 2. Actually three type of compounds can be isolated from both reactions, namely  $[\text{Mn}_2(\mu\text{-H})(\mu\text{-}\sigma\text{-R-C}\equiv\text{CR})(\text{CO})_6(\text{dppm})]$ , 3,  $[\text{Mn}_2(\mu\text{-HC}\equiv\text{C-t-Bu})(\text{CO})_6(\text{dppm})]$ , 4, and  $[\text{Mn}(\text{CO})_3(\mu\text{-dppm})(\mu\text{-OC(MeO)C}\equiv\text{CH})\text{Mn}(\text{CO})_3]$ , 5. On the other hand the vinyl compound  $[\text{Mn}_2(\mu\text{-H})(\mu\text{-HC=CH}_2)(\text{CO})_6(\text{dppm})]$ , 6, is only accesible from 1 and finally  $[\text{Mn}(\text{CO})_4(\mu\text{-dppm})\text{Mn}(\eta^3\text{-C(O)CH=CR})\text{-(CO)}_2]$ , 7, is exclusively obtained in the reactions of 2 with  $\text{HC}\equiv\text{CR}$ , ( $\text{R} = \text{H}, \text{CH}_2\text{OCH}_3$ ).

## NEW ORGANOMETALLIC RHENIUM CLUSTER COMPOUNDS

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\* Dipartimento di Chimica Inorganica e Metallorganica, V.Venezian 21, 20133 Milano.

\* Istituto di Chimica Strutturistica Inorganica, V.Venezian 21, 20133 Milano

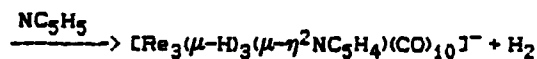
The unsaturated triangular cluster anion<sup>1</sup>  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$  provides a good entry into the organometallic chemistry of hydrido-carbonyl clusters of rhenium, by reactions such as:

(a) hydride transfer to an electrophilic site of an unsaturated organic molecule:



Similar reactions have been previously observed with tropylium ion<sup>2</sup> and acetone<sup>3</sup>.

(b)  $\text{H}_2$  elimination and oxidative addition of a CH bond of a coordinated pyridine molecule:



(c) nucleophilic attack on a carbonyl ligand, followed by hydride transfer on the carbon atom

(a reaction analogous to that<sup>4</sup> previously observed with  $\text{LiHBR}_3$ ):

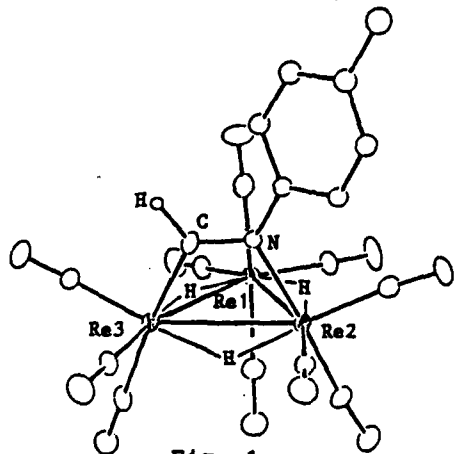
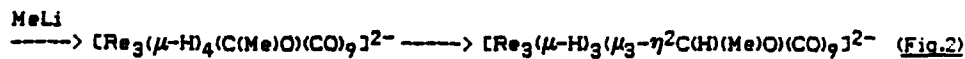


Fig. 1

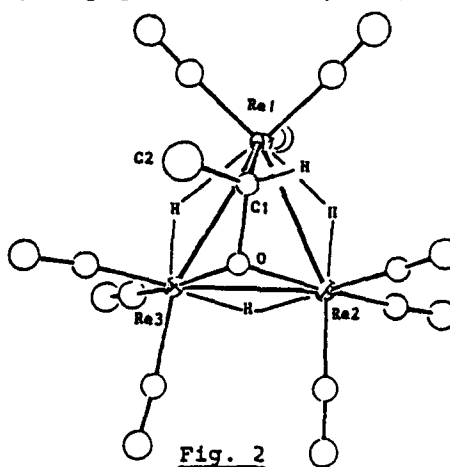


Fig. 2

Work supported by Centro CNR Sintesi Struttura Composti Metalli di Transizione of Milan.

1) T. Beringhelli, G. Ciani, G. D'Alfonso, H. Molinari and A. Sironi, *Inorg. Chem.*, 1985, 24, 2666.

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4) T. Beringhelli, G. D'Alfonso, G. Ciani and H. Molinari, *Organometallics*, 1987, 6, 194.

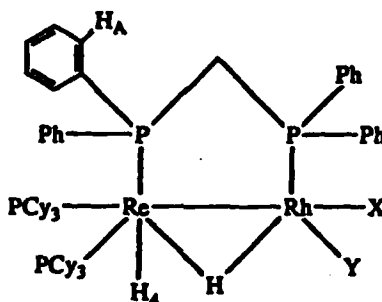


# Systematic Syntheses of Polyhydrido Heterobimetallics Containing Bridging Diphosphines

Stuart Carr, Xavier Fontaine, Edmund Fowles, Bernard Shaw and Mark Thornton-Pett; Department of Inorganic and Structural Chemistry, University of Leeds, Leeds, LS2 9JT, UK

We have found that treatment of  $[\text{ReH}_7(\text{PCy}_3)_2]$ ,  $[\text{OsH}_6(\text{PCy}_3)]$  or  $[\text{IrH}_5(\text{PCy}_3)_2]$  ( $\text{PCy}_3$  = tricyclohexylphosphine) with diphosphines gave complexes of the type  $[\text{MH}_x(\text{PCy}_3)_2(\text{L-L})]$  ( $\text{MH}_x$  =  $\text{ReH}_5$ ,  $\text{OsH}_4$  or  $\text{IrH}_3$ ;  $\text{L-L}$  = a monodentate diphosphine such as  $\text{PPh}_2\text{CH}_2\text{PPh}_2$ ,  $\text{PPh}_2\text{C}(\text{=CH}_2)\text{PPh}_2$ ,  $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$  or *cis*- $\text{PPh}_2\text{CH=CHPPh}_2$ ). Complexation of the free end of the diphosphine with other metals e.g. Cu, Ag, Mn, Rh or Ir gave heterobimetallic complexes which contained both terminal and bridging hydrides. These were fluxional at room temperature. Thus treatment of  $[\text{ReH}_5(\text{PCy}_3)_2(\text{PPh}_2\text{C}(\text{=CH}_2)\text{PPh}_2)]$  with  $[\text{RhCl}(\text{CO})_2]_2$  or  $[\text{RhCl}(\text{norbornadiene})]_2$  gave respectively (1) or (2):

- (1) X, Y = CO, Cl  
(2) X, Y = norbornadiene<sup>+</sup>



The hydride ligands in (1) and (2) were static at  $-80^\circ\text{C}$  and these complexes were each a mixture of two isomers which rapidly interconverted at room temperature. Evidence is given for an interesting interaction between  $\text{H}_A$  and Rh. Other reactions will be described.

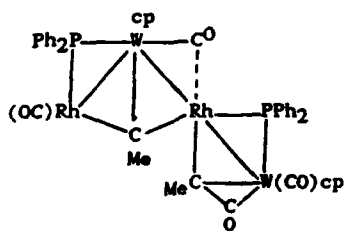
# SYNTHESIS OF 'CHAIN'-TYPE POLYNUCLEAR METAL COMPLEXES CONTAINING TUNGSTEN AND RHODIUM OR IRIUM

Simon J. Davies, Judith A.K. Howard, Max U. Pilotti, and F. Gordon A. Stone,

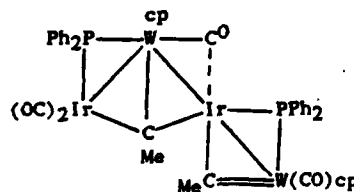
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, Great Britain.

We have recently illustrated the rational directed syntheses of novel transition metal cluster compounds containing open chains of molybdenum or tungsten and nickel or platinum atoms, bridged by alkylidyne ligands. In an attempt to prepare similar compounds containing rhodium the reaction between  $[\text{Rh}(\text{cod})(\mu\text{-PPh}_2)_2]$  (1) and  $[\text{W}(\text{=CMe}(\text{CO})_2)(\eta\text{-C}_5\text{H}_5)]$  (2) was investigated.

The initial product of the reaction is  $[\text{Rh}_2\text{W}_2(\mu\text{-C}(\text{Me})\text{C}(\text{O}))(\mu_3\text{-CMe})(\text{CO})_3(\mu\text{-PPh}_2)_2(\eta\text{-C}_5\text{H}_5)_2]$  (3).



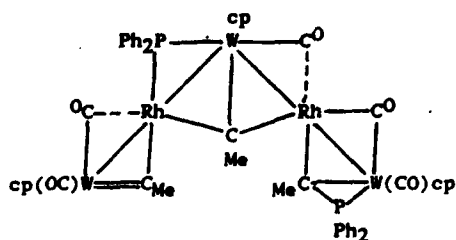
(3)



(5)

In contrast (2) reacts with  $[\text{Ir}(\text{cod})(\mu\text{-PPh}_2)_2]$  (4) to give the related compound  $[\text{Ir}_2\text{W}_2(\mu\text{-CMe})(\mu_3\text{-CMe})(\text{CO})_4(\mu\text{-PPh}_2)_2(\eta\text{-C}_5\text{H}_5)_2]$  (5).

Compound (3) reacts with excess (2) to give the pentanuclear complex  $[\text{Rh}_2\text{W}_3(\mu\text{-C}(\text{Me})\text{C}(\text{O}))(\mu\text{-CMe})(\mu_3\text{-CMe})(\text{CO})_4(\mu\text{-PPh}_2)_2(\eta\text{-C}_5\text{H}_5)_3]$  (6) which isomerises slowly in solution to yield  $[\text{Rh}_2\text{W}_3(\mu\text{-CO})(\mu\text{-C}(\text{Me})\text{PPh}_2)(\mu\text{-CMe})(\mu_3\text{-CMe})(\text{CO})_4(\mu\text{-PPh}_2)(\eta\text{-C}_5\text{H}_5)_3]$  (7) whose structure has been determined by X-ray analysis.



(7)

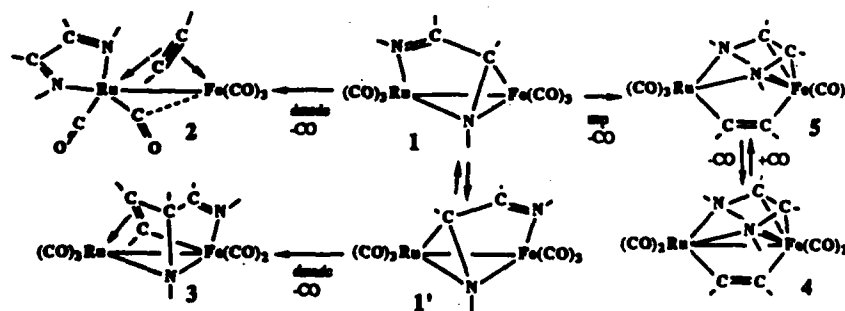
## Reference

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**THE REACTIVITY OF THE HETERODINUCLEAR  $\alpha$ -DIIMINE COMPLEX  
 $\text{FeRu}(\text{CO})_6(\text{iPr-N}=\text{CHCH}=\text{N-iPr})$  TOWARDS ALKYNES**

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In order to compare the reactivity of homo- and heterodinuclear  $\alpha$ -diimine complexes towards alkynes the novel heterodinuclear complex  $\text{FeRu}(\text{CO})_6(\text{iPr-DAB})$  (**1**) [ $\text{iPr-DAB} = \text{iPr-N}=\text{CHCH}=\text{N-iPr}$ ], with the  $\alpha$ -diimine bonded as a  $\sigma\text{-N}, \mu_2\text{-N}', \eta^2\text{-C}=\text{N}'$  bridging 6e donor, was synthesized. Reaction of **1** with  $\text{MeOC}(\text{O})\text{C}\equiv\text{CC}(\text{O})\text{OMe}$  (*dmadc*) yields two products:  $\text{FeRu}(\text{CO})_5(\sigma, \sigma\text{-N}, \text{N}'\text{-iPr-DAB})(\mu_2, \eta^2\text{-dmadc})$  (**2**), which has a chelating *iPr-DAB* on Ru as well as a perpendicular bridging alkyne, and  $\text{FeRu}(\text{CO})_5[\text{iPr-N}=\text{CHCH}(\text{N-iPr})\text{-C}(\text{C}(\text{O})\text{OMe})=\text{CC}(\text{O})\text{OMe}]$  (**3**) (X-ray). Complex **2** is formed via the substitution of the  $\eta^2\text{-C}=\text{N}$  bonded imine moiety (to Fe) in **1** by an  $\eta^2\text{-C}\equiv\text{C}$  bonded alkyne, followed by the loss of one CO. This type of mechanism is also involved in the reaction of  $\text{Fe}_2(\text{CO})_6(\text{iPr-DAB})$  with *dmadc*. The organic ligand in **3** results from the C-C coupling of one of the DAB imine C atoms and the alkyne. This C-C coupling is probably preceded by an isomerization of **1** ( $\eta^2\text{-C}=\text{N}$  coordination to Fe) to give the intermediate **1'** with  $\eta^2\text{-C}=\text{N}$  coordination to Ru. The C-C coupling of the alkyne with the  $\pi$ -bonded imine C atom in **1'** followed by the loss of one CO yields **3**. An analogous C-C coupling occurs in the reaction of  $\text{Ru}_2(\text{CO})_6(\text{iPr-DAB})$  with *dmadc*. These results lead to the conclusion that the nature of the  $\eta^2\text{-C}=\text{N}$ -metal interaction has a major influence on the path along which the reactions of  $\text{M}_2(\text{CO})_6(\text{iPr-DAB})$  [ $\text{M}_2 = \text{Fe}_2, \text{FeRu}, \text{Ru}_2$ ] proceed. A third process is illustrated by the formation of  $\text{FeRu}(\text{CO})_5(\text{iPr-DAB})(\mu_2\text{-mp})$  (**5**) (X-ray) from **1** and  $\text{MeOC}(\text{O})\text{C}\equiv\text{CH}$  (*mp*) which involves the insertion of the alkyne in the Fe-Ru bond followed by the loss of one CO. Complex **5** loses easily and reversibly one CO to give  $\text{FeRu}(\text{CO})_4(\text{iPr-DAB})(\mu_2\text{-mp})$  (**4**). In both **4** and **5** the DAB ligand is bonded as a  $\sigma, \sigma\text{-N}, \text{N}'\text{-}\eta^2, \eta^2\text{-C}=\text{N}, \text{C}=\text{N}'$  bridging 8e donor. Products of type **4** have also been found in reactions of the  $\text{Fe}_2$  and  $\text{Ru}_2$  analogues with alkynes.



## CARBON-HYDROGEN AND CARBON-NITROGEN ACTIVATION PROCESSES

IN THE REACTIONS OF  $\text{Ru}_3(10)_{12}$  WITH TERTIARY AMINES

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Robert W. Gellert, Department of Chemistry, California State University, Los Angeles, California 90024

The reactions of tertiary amines,  $\text{NR}_2\text{R}'$  ( $\text{R} = \text{CH}_2\text{CH}_3$ ,  $\text{CH}(\text{CH}_3)_2$ ;  $\text{R}' = \text{CH}_2\text{CH}_3$ ) with  $\text{Ru}_3(\text{CO})_{12}$  promoted by the radical catalyst  $[\text{Fe}(\mu\text{SCH}_2\text{CCH}_3)(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3]_2$  have been examined. The structures of the major triruthenium products have been determined by x-ray diffraction and multinuclear nmr studies. In the case of  $\text{N}(\text{CH}_2\text{CH}_3)_3$ <sup>1</sup> three major  $\text{Ru}_3$  products are obtained which result from a combination C-H and C-N cleavage reactions and one product which is the result of insertion of a  $\text{C}_2$  fragment into the tertiary amines. With the bulkier  $\text{N}(\text{CH}(\text{CH}_3)_2)_2(\text{CH}_2\text{CH}_3)$  only two major  $\text{Ru}_3$  containing complexes are isolated which are the result of only C-H cleavage reactions on the ethyl group of the amine. In both series of complexes structures containing zwitterionic carbon nitrogen double bonds both coordinated to the cluster or as a pendent ligand are observed.<sup>2</sup> The importance of this type of bonding in C-N cleavage processes and a general scheme for the sequence of and factors controlling C-H and C-N bond cleavage processes will be presented based on the structural work and on the observed interconversion of the various products obtained.

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PYROLYSIS OF  $\text{Os}_3(\text{CO})_{10}(\text{R}_2\text{C}_2)$  ( $\text{R}=\text{Ph}, \text{Me}$ )

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Pyrolysis of  $\text{Os}_3(\text{CO})_{10}(\text{R}_2\text{C}_2)$  ( $\text{R}=\text{Ph}, \text{Me}$ ) gives a range of products. At high temperature ( $265^\circ\text{C}$ ), the dianion  $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$  is obtained as a major product, while at lower temperature ( $210^\circ\text{C}$ ), several neutral complexes are obtained including some high nuclearity clusters. These include  $\text{Os}_4(\text{CO})_{12}(\text{Ph}_2\text{C}_2)$  (1),  $\text{HOs}_7(\text{CO})_{18}[\text{PhCC}(\text{C}_6\text{H}_4)]$  (2),  $\text{HOs}_3(\text{CO})_9(\text{C}_4\text{H}_5)$  (3),  $\text{HOs}_4(\text{CO})_{11}(\text{C}_4\text{H}_5)$  (4),  $\text{Os}_4(\text{CO})_{12}(\text{C}_4\text{H}_6)$  (5). All these compounds have been identified and characterised by i.r., mass spectroscopy and  $^1\text{H}$  n.m.r. spectroscopy. Among these, compounds (2) and (4) have not been reported so far.  $^1\text{H}$  n.m.r. studies of these two compounds give evidence for orthometallation of a phenyl ligand in (2), and an allylic bonding mode in (4) due to ligand rearrangement. Compounds (3) and (5) may be new isomers of the known compounds, as suggested by  $^1\text{H}$  n.m.r. evidence<sup>1,2</sup>. The X-ray crystallographic study of (3) is in progress.

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OXIDATIVE ADDITION OF VINYL-DIPHENYL-PHOSPHINE ON  $\text{Ru}_3(\text{CO})_{12}$ . CHARACTERIZATION AND CRYSTAL STRUCTURE OF  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH=CH}_2)(\mu, \eta^2\text{-PPh}_2\text{CH=CH})$ .

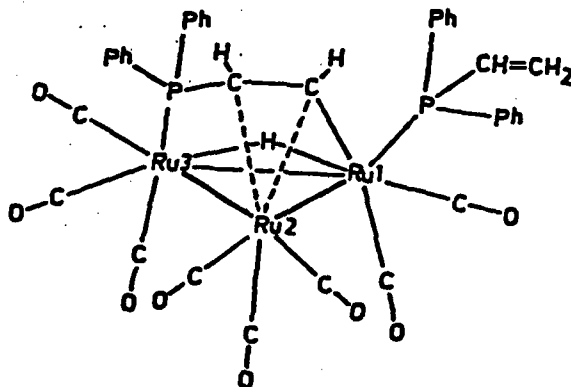
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The title complex (1), obtained by reacting  $\text{Ru}_3(\text{CO})_{12}$  with vinyl-diphenyl-phosphine in aliphatic hydrocarbons under moderate heat, has been characterized by multinuclear n.m.r. spectroscopy. The structure of 1, fully elucidated by X-ray diffraction methods, is represented in the Figure.

The complex 1 represents an example of oxidative addition, without P-C bond cleavage, involving a phosphine characterized by an unsaturated hydrocarbyl substituent; generally, indeed, phosphino-alkynes undergo P-C bond cleavage even in mild conditions.<sup>1,2</sup> Upon thermal treatment, 1 gives several phosphido-bridged derivatives, which are now under investigation.



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Reactions of Trinuclear (Ru and Os) Carbonyl Clusters with Amino-Alcohols and -Thiols.

Silvio Aime, Mauro Botta, Roberto Gobetto, Luciano Milone, Domenico Osella and Luciana Violano

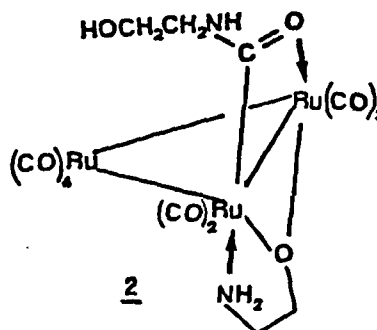
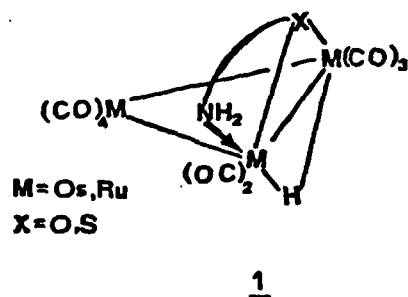
Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 7/9, 10125 Torino, Italy

In the study of these reactions under different experimental conditions we were able to isolate and characterize several organometal carbonyl clusters corresponding both to the oxidative addition of -OH, -SH and -NH bonds to the metallic moiety and to the nucleophilic attack of the  $\text{NH}_2$  group on coordinated CO ligands as already found in the interaction of primary and secondary amines with  $\text{M}_3(\text{CO})_{12}$  clusters ( $\text{M}=\text{Ru}$  and  $\text{Os}$ )<sup>1,2,3</sup>.

When the oxidative addition reaction involves the oxygen or sulphur centres the resulting derivatives contain the  $\text{NH}_2$  group coordinating one of the metal atoms bridged by the heteroatom as shown in 1. The easy cleavage of the coordinative bonds to form unsaturated species in solution under mild experimental conditions shows interesting properties for these organometallic coordination compound.

In the reaction between  $\text{Ru}_3(\text{CO})_{12}$  and Ethanolamine (ETA) in THF as solvent at ambient temperature a single product is obtained (isolated in 65% yield) which contains two ETA moieties bonded as shown in 2.

This work was supported by Italian Ministry of Education.



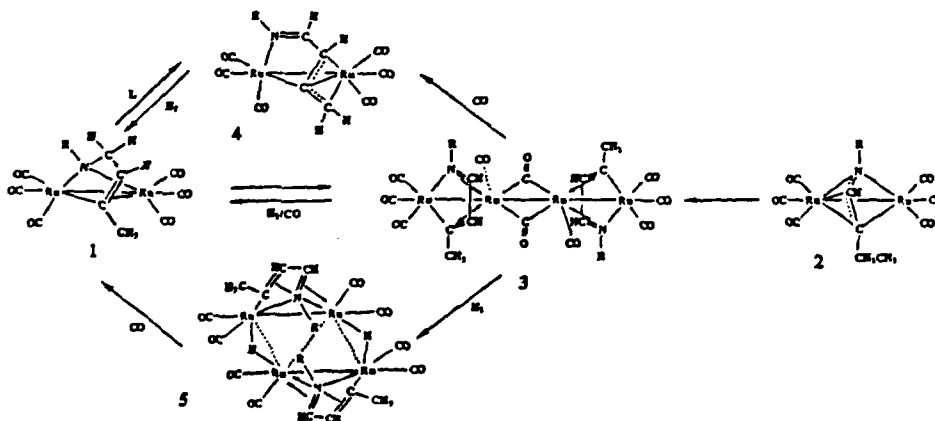
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**Hydrogenation and dehydrogenation processes on  
di- and tetranuclear ruthenium compounds**

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Whereas the coordination and reactivity of 1,3-dienes and 1,4-diaza-1,3-dienes on metal carbonyl frameworks of the Iron triad has been extensively investigated, the chemistry of 1-aza-1,3-dienes remained virtually unexplored. Only in the last few years this gap has partly been filled up. New di-, tri- and tetranuclear organometallic compounds containing one or two ligands arising from hydrogen migration or abstraction were isolated from thermal reactions of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{CH}_3\text{-CH=CH-CH=N-R}$  ( $\text{R=i-Pr}$ ,  $\text{c-Hex}$ ,  $\text{t-Bu}$ ). On the poster we present additional information about their formation and interconversion and the influence of the R-group.

The dinuclear compounds **1** ( $\text{R=i-Pr}$ ,  $\text{c-Hex}$ ) and **2** ( $\text{R=i-Pr}$ ,  $\text{c-Hex}$ ,  $\text{t-Bu}$ ) are initially formed. A sequence of thermal reaction steps including dehydrogenation of the ligands, loss of CO from the metal framework and subsequent dimerization results in the almost quantitative formation of the tetranuclear **3** after 4-24 h (**1**) or 3-4 days (**2**). In a reverse reaction hydrogenation of **3** in the presence of CO yields **1**. In the latter two different reaction pathways may be involved with the intermediacy of **4** or **5**. Dehydrogenation of **1** is also observed during thermal reactions in the presence of an excess of 1-aza-1,3-diene, though another reaction is kinetically favoured, which results in the formation of **4**. Possible mechanisms and catalytic applications will be discussed.





<sup>1</sup>H Spin-Lattice Relaxation Times in Hydrido Carbonyl Clusters as an Aid to the determination of Molecular Structures

Silvio Aime, Mauro Botta, Marco Cisero, Roberto Gobetto, Luciano Milone and Domenico Osella

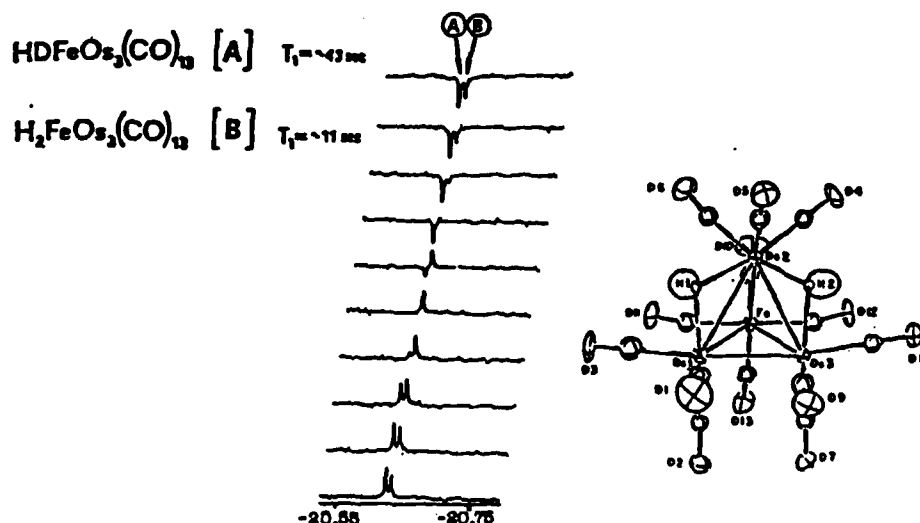
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This work deals with the evaluation of H-H distances obtained via the measurement of proton spin-lattice relaxation times:

$$\frac{1}{T_1} = \frac{1}{2} \cdot \frac{\gamma^4 \hbar^2}{r^6} \cdot \tau_c$$

The molecular correlation time  $\tau_c$  has been evaluated from  $T_1$  and n.O.e. determinations of rigid C<sup>13</sup>H fragment in the organic ligand or by applying the Stokes-Debye formula.

In systems containing two chemically and magnetically equivalent hydrides (and no other hydrogen) it is possible to extract structural distances by evaluating the difference in the relaxation rates between the two H,H and H,D isotopomers if  $\tau_c$  is known by an independent experiment. The measurement of the relaxation times  $T_1$  of the two isotopomers is possible in the same experiment by making use of the small isotopic shift between the hydrido resonances of the two isotopomers. This is shown in the figure for  $H_2FeOs_3(CO)_{13}$  and  $HDFeOs_3(CO)_{13}$ .



This work was supported by Italian C.N.R. under the grant no. 87.007.03.

## BUILD UP OF OSMIUM CARBONYL CLUSTERS USING ARSENIC LIGANDS

Karlheinz Guldner, Brian F.G. Johnson, Jack Lewis, Anju D. Massey.

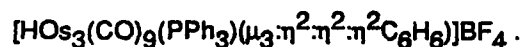
University Chemical Laboratory, Lensfield Road. Cambridge CB2 1EW. U.K.

Reaction of the activated cluster  $\text{Os}_3(\text{CO})_{12-n}(\text{NCMe})_n$  ( $n=1$  (1a),  $n=2$  (1b)) with primary arsines<sup>1</sup> ( $\text{RAsH}_2$ ,  $\text{R}=\text{Ph, Me, H}$ ) yields the arsinidene compounds  $\text{H}_2\text{Os}_3(\text{CO})_{11}(\mu_3\text{-AsR})$  (2a) ( $\text{R}=\text{Ph, Me, H}$ ). At elevated temperatures, (2a) is transformed to the AsPh capped cluster  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-AsPh})]$  (2b). Treatment of (2a) with osmium sources like  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{H}_2\text{Os}(\text{CO})_4$  and  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  under thermolytic conditions gives the tetranuclear cluster  $[(\mu\text{-H})_2\text{Os}_4(\text{CO})_{12}(\mu_3\text{-AsPh})]$  (2c) and the pentanuclear cluster  $[(\mu\text{-H})_2\text{Os}_5(\text{CO})_{15}(\mu_4\text{-AsPh})]$  (2d) as the major products. Similarly the reaction of (1a) and (1b) with the secondary arsine<sup>2</sup>  $\text{Me}_2\text{AsH}$  gives the AsMe<sub>2</sub> bridged triosmium clusters  $[(\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-AsMe}_2))]$  (2e) and  $[(\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu\text{-AsMe}_2)_2)]$  (2f) which are formed via the intermediate compound  $\text{Os}_3\text{H}(\text{CO})_{11}(\mu\text{-AsMe}_2)$  (2g).

Extension of this work using  $\text{AsH}_3$ ,  $\text{PhAsH}_2$  and  $\text{As}(\text{p-Tol})_3$  ligands leads to the synthesis of osmium clusters, ranging in nuclearity from three to six metal atoms, containing  $\mu\text{-AsR}$ ,  $\mu\text{-AsR}_2$  and  $\text{AsR}_3$  groups. The reaction of (1a) with  $\text{PhAsH}_2$  in refluxing  $\text{CH}_2\text{Cl}_2$  gives  $\text{Os}_3(\text{CO})_9(\text{AsPh})_2$  (3a). In comparison, the reaction with  $\text{As}(\text{p-Tol})_3$  gives  $\text{Os}_3(\text{CO})_9(\mu\text{-AsC}_6\text{H}_4\text{CH}_3)(\mu\text{-C}_6\text{H}_3\text{CH}_3)$  (4a), which results from the migration of one tolyl group from the arsenic to the cluster framework, and  $\text{Os}_3(\text{CO})_{10}(\mu\text{-AsC}_6\text{H}_4\text{CH}_3)(\mu\text{-C}_6\text{H}_3\text{CH}_3)$  (4b). Reaction of  $\text{As}(\text{p-Tol})_3$  with (1b) gives a trinuclear osmium cluster with two bridging arsine ligands and involves metal-metal bond breakage (4c). Cluster build-up reactions using the arsine substituted cluster  $\text{Os}_3(\text{CO})_{11}\text{AsTol}_3$  with  $\text{H}_2\text{Os}(\text{CO})_4$  gives  $\text{Os}_4(\text{CO})_{11}\text{As}_2\text{Tol}_2$  (5a) and  $\text{Os}_6(\text{CO})_{13}\text{As}_2\text{Tol}_2$  (5b). A hexanuclear cluster  $\text{H}_2\text{Os}_6(\text{CO})_{21}\text{AsH}$  (6a) is also obtained by reacting  $\text{Os}_3(\text{CO})_{11}\text{AsH}_3$  with (1a). All these compounds have been characterised by i.r., n.m.r and mass spectroscopy. The X-ray crystallographic study of (4a) and (4c) is in progress.

Reference: 1,2: Karlheinz Guldner, Brian F.G. Johnson, Jack Lewis and Paul R. Raithby. (Unpublished results).

Arene Activation by Triosmium Cluster: Nucleophilic Addition to cationic



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The ability of certain transition metal centers to activate normally unreactive  $\pi$ -hydrocarbons towards nucleophilic attack has been known for several decades (1). This area has attracted considerable interest in recent years due to its potential application in organic synthesis.

Factors controlling reactivity, mechanism and site of nucleophilic addition in mononuclear metal-arene systems have been reviewed(1) and analogous studies concerning the electrophilicity of benzene and toluene, coordinated in the face-capping bonding mode, in  $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{C}_6\text{H}_6)]$  and  $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2(\text{C}_6\text{H}_5\text{Me}))]$  have recently been performed(2).

The present work is concerned with nucleophilic addition to the benzene in  $[\text{HOs}_3(\text{CO})_8(\text{PPh}_3)(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{C}_6\text{H}_6)]\text{BF}_4$ . Reaction with diethylamine, MeLi, PhLi,  $\text{H}^-$ ,  $\text{MeO}^-$  and DBU afforded neutral compounds. NMR evidence indicates attack occurs at the arene ring and this has been confirmed by a X-ray structural analysis of  $[\text{HOs}_3(\text{CO})_8(\text{PPh}_3)(\mu_3\text{-}\eta^2\text{-}\eta^1\text{-}\eta^2\text{C}_6\text{H}_7)]$ .

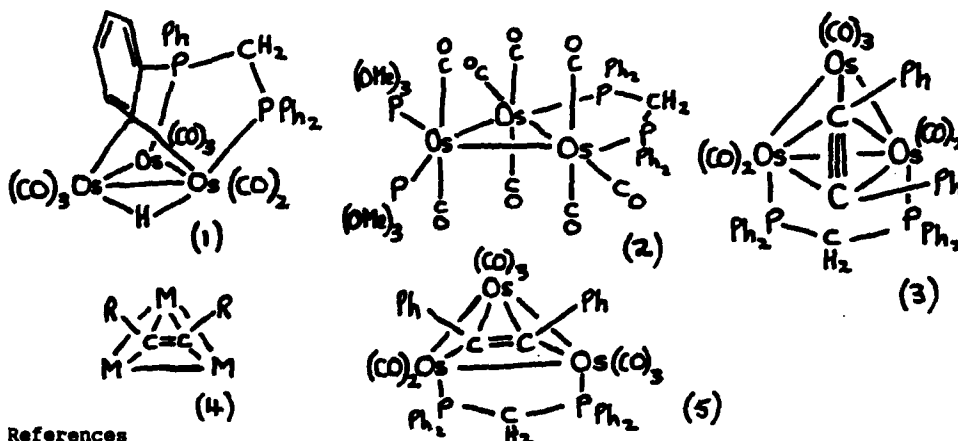
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ELECTRONIC CONTROL OF THE COORDINATION MODE OF AN ALKYNE  
TO A TRI-OSMIUM CLUSTER AND THE REACTIVITY OF THE  
UNSATURATED CLUSTER  $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4)]$

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The unsaturated cluster  $[\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4)]$  (1) readily undergoes a de-metallation reaction, allowing the addition of two or four electrons to the cluster framework to occur under mild conditions. For example, complex (1) reacts with  $\text{P(OMe)}_3$  at room temperature to produce  $[\text{Os}_3(\text{CO})_9(\text{dppm})(\text{P(OMe)}_3)_2]$  (2) ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ). With the alkyne,  $\text{PhC}\equiv\text{CPh}$ , complex (1) reacts to give the 46-electron cluster  $[\text{Os}_3(\text{CO})_9(\text{dppm})(\text{PhC}\equiv\text{CPh})]$  (3), in which the alkyne ligand is coordinated in the  $\mu_3, \eta^2-\parallel$  mode (shown by X-ray crystallography).<sup>2</sup> This coordination mode, previously unknown for triosmium clusters, is favoured over the usual  $\mu_3, \eta^2-\parallel$  mode (4) by the presence of the  $\sigma$ -donating diposphine ligand, and demonstrates how a change in electronic properties of a triangular array of metal atoms can influence the mode of coordination of unsaturated organic molecules to that array.

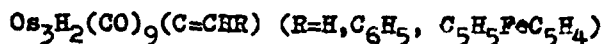
The cluster (3) also undergoes a ready reversible addition of CO leading to the formation of  $[\text{Os}_3(\text{CO})_{10}(\text{dppm})(\text{PhC}\equiv\text{CPh})]$  (5), in which the coordination of the alkyne is changed to the more usual  $\mu_3, \eta^2-\parallel$  mode.



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## PROTONATION OF ALKENYLIDENE COMPLEXES



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Reaction of  $\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}=\text{CHR})$  (Ib,c R= $\text{C}_6\text{H}_5$ ,  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ ) in  $\text{CD}_2\text{Cl}_2$  with  $\text{CF}_3\text{COOH}$  at low temperatures affords bridged alkenyl complexes  $\text{Os}_3\text{H}_2(\text{CO})_9(\text{CH}=\text{CHR})\{\text{OC}(\text{O})\text{CF}_3\}$  (IIb,c) which were characterized by  $^1\text{H}$ ,  $^{19}\text{F}$  NMR and IR spectroscopy. At room temperature complexes IIb,c rearrange to the corresponding cationic trihydrides  $[\text{Os}_3\text{H}_3(\text{CO})_9(\text{C}=\text{CHR})]^+$  (IIIb,c) by alkenyl hydrogen atom migration to the trimetallic core.

Whereas protonation of Ib,c with  $\text{CF}_3\text{COOH}$  at  $-30^\circ\text{C}$  occurs via attack on the carbene atom of alkenylidene ligand, the reaction of  $\text{Os}_3\text{H}_2(\text{CO})_9(\text{C}=\text{CH}_2)$  (Ia) under the same conditions gives only  $[\text{Os}_3\text{H}_3(\text{CO})_9(\text{C}=\text{CH}_2)]^+$  (IIIa), and there is no evidence for the formation of a bridged alkenyl complex.

Treatment of Ia-c with  $\text{HBF}_4 \cdot \text{OEt}_2$  in  $\text{CD}_2\text{Cl}_2$  even at  $-60^\circ\text{C}$  afforded only cationic trihydrides IIIa-c.

## SYNTHESIS AND PROPERTIES OF IRON GROUP METAL CLUSTERS

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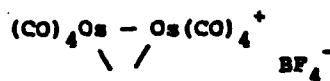
Krivykh Vasily and Rybinskaya Margarita, A.N. Nesmeyanov  
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Thermal and photochemical reactions of trinuclear carbonyls  
of Fe, Ru and Os with allyl alcohol in acidic medium as well  
as their reactions with  $(\text{CH}_3)_3\text{NO} \cdot 2 \text{H}_2\text{O}$  with subsequent  
protonation have been reported.<sup>1)</sup>

Cationic mononuclear allyltetracarbonyl complexes of Fe, Ru,  
Os and cationic Os cluster with  $\pi$ -allyl ligand have been  
obtained. In case of  $\text{Os}_3(\text{CO})_{12}$  the formation of the two  
compounds, namely, mono- and trinuclear (III and IV) cationic  
allyl complexes were observed:



III



IV

Formation and structural characterization by means of IR and  
NMR methods as well as by X-ray methods will be presented and  
discussed. The properties of the complexes will be reported.

1. V.V. Krivykh, T. Asunta, O.V. Gusev and M.I. Rybinskaya,  
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THE CHEMISTRY OF THE HYDRIDOCARBONYLTRIOSMIUM  
ANION  $[\text{HOs}_3(\text{CO})_{11}]^-$

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For the past few years the study of mixed-metal clusters have been intensive and since then numerous mixed-metal clusters have been synthesised. The study of such cluster is interesting as it throw light into the understanding of catalytic activities of bimetallic heterogenous catalysts.

There are several methods of preparing mixed-metal clusters such as pyrolysis of transition metal carbonyls, addition of coordinatively unsaturated species, redox condensation and reaction of carbonylmetalates with metal halides. Herein we report the synthesis of goldtriosmium clusters using the anion  $[\text{HOs}_3(\text{CO})_{11}]^-$  as precursor.

The reaction of the anion  $[\text{HOs}_3(\text{CO})_{11}]^-$  with an equivalent amount of  $\text{R}_3\text{PAuCl}$  in dichloromethane at room temperature lead to the monogold clusters  $\text{HOs}_3(\text{CO})_{11}\text{AuPR}_3$  and  $\text{HOs}_3(\text{CO})_{10}\text{AuPPh}_3$ <sup>1</sup>. When the anion  $[\text{HOs}_3(\text{CO})_{11}]^-$  is refluxed with a two-fold equivalent amounts of  $\text{R}_3\text{PAuCl}$  in chloroform the digold cluster  $\text{Os}_3(\text{CO})_{10}(\text{AuPR}_3)_2$  is obtained in high yield<sup>2</sup>. Stirring the anionic cluster  $[\text{HOs}_3(\text{CO})_{11}]^-$  with half equivalents of  $\text{R}_3\text{PAuCl}$  in chloroform at room temperature afforded the bridged-gold cluster  $[(\text{HOs}_3(\text{CO})_{10})_2\text{Au}]^{-3}$ . The yield of the goldtriosmium clusters is further enhanced in presence of  $\text{TiPF}_6$ .

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<sup>3</sup> B.F.G. Johnson, D.A. Kaner, J. Lewis and P.R. Raithby, J.Chem.Soc., Chem.Comm., 753, 1981.

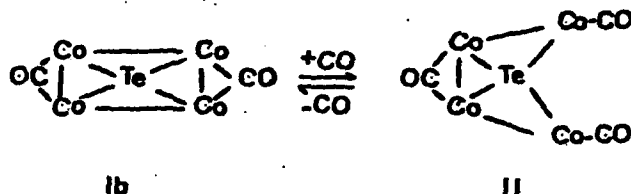
TETRACOBALT PLANAR CLUSTERS WITH  $\mu_4$ -BRIDGING LIGANDS

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The core structures of tetranuclear clusters have mainly tetrahedral or butterfly shapes, whereas the square or rectangular planar arrays are quite rare. Among them, few examples of cobalt carbonyls are known, of general formula  $\text{Co}_4(\text{CO})_8(\mu\text{-CO})_2(\mu_4\text{-X})(\mu_4\text{-Y})$  and of similar structure, where  $\text{X}=\text{Y}=\text{S}$  (Ia),  $\text{Te}$  (Ib),  $\text{PC}_6\text{H}_5$  (Ic) are coordinated on the two sides of the rectangular  $\text{Co}_4$  core and two CO groups bridge the short Co-Co bonds. We report the synthesis of complex Id with  $\text{X}=\text{Y}=\text{Se}$  via a room temperature reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{CSe}_2$  or red Se and its structure determination. Comparing the dichalcogen compounds, the dimensions of the  $\text{Co}_4$  rectangle regularly increase in the order  $\text{S} < \text{Se} < \text{Te}$ , for allocating the greater bridging chalcogen atoms; the Co-X and the non-bonding X...Y distances increase in the same way.

Complex Ib adds reversibly a CO molecule to give  $\text{Co}_4(\text{CO})_{10}(\mu\text{-CO})(\mu_4\text{-Te})_2$  (II). An easy high yield synthesis of II by reacting  $\text{Co}_2(\text{CO})_8$  with  $[\text{TeO}_3]^{2-}$  at room temperature and atmospheric pressure was carried out and the complex completely characterized.



The  $\text{Co}_4$  core of II remains planar with trapezoidal shape, the three Co-Co bond distances being similar and close to the CO-bridged distances in Ib.

New complexes Ia ( $\text{X}=\text{S}$ ,  $\text{Y}=\text{HC}_2\text{C}_6\text{H}_5$ ) and If ( $\text{X}=\text{S}$ ,  $\text{Y}=\text{HC}_2\text{H}$ ) were prepared in good yields by reacting  $\text{Co}_3(\text{CO})_9\text{S}$  with the alkyne in the presence of  $(\text{CH}_3)_3\text{NO}$ . The reaction is a noteworthy example of cluster expansion, which usually begins by a decarbonylation process largely favoured by  $(\text{CH}_3)_3\text{NO}$ . The structure of Ia shows a quite uncommon coordination of an alkyne to a planar  $\text{M}_4$  core with the  $\text{C}\equiv\text{C}$  bond parallel to the long side of the rectangle. The i.r. frequency of the acetylene modes in If were assigned and related to the type of the alkyne-cluster bonding.



## MONONUCLEAR THIOLATECOBALT CARBONYLS: CLUSTER BUILDING BLOCKS

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$\text{RCo}(\text{CO})_4$  ( $\text{R}=\text{Et}$ ,  $\text{PhCH}_2$ ,  $\text{Ph}$ ) (1) compounds were prepared from  $\text{RNa}$  and  $\text{ICo}(\text{CO})_4$  or  $\text{Co}_2(\text{CO})_8$  and from  $\text{RSSR}$  and  $\text{Na/Co}(\text{CO})_4$  /.

These very instable compounds react with  $\text{PPh}_3$  to give  $\text{RCo}(\text{CO})_3(\text{PPh}_3)$  (2) which can be isolated. 1 readily oligomerizes to  $\text{Co}_3$  to  $\text{Co}_6$  cluster derivatives already over  $-20^\circ\text{C}$ . In contrast to the (hypothetic)  $\text{ROCo}(\text{CO})_4$  alkoxides 1 does not react with  $\text{CO}$  up to 15 bar at  $-30^\circ\text{C}$ .

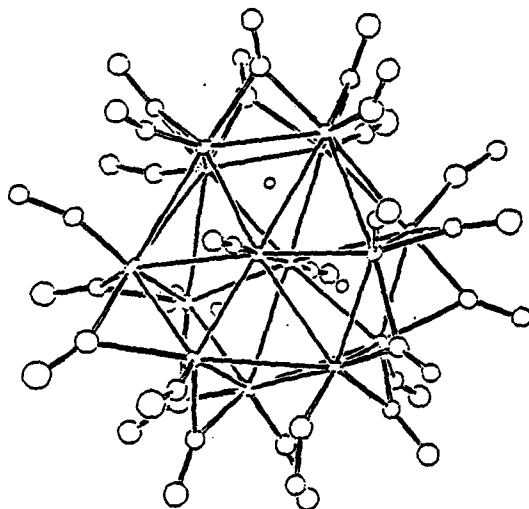
The phosphine complexes 2 react to  $\text{PPh}_3$  containing cluster derivatives which are in course of characterization.

NEW HIGH NUCLEARITY COBALT NITRIDO-CARBONYL CLUSTERS. SYNTHESIS  
AND X-RAY STRUCTURE OF THE ANION  $[\text{Co}_{14}\text{N}_3(\text{CO})_{28}]^{3-}$ .

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In 1979 we reported the first examples of carbonyl cluster compounds containing a fully encapsulated nitrogen atom, namely the trigonal prismatic anions  $[\text{M}_6\text{N}(\text{CO})_{15}]^-$  ( $\text{M} = \text{Co}, \text{Rh}$ ).<sup>1</sup> Mild pyrolysis of these species gave rise, in the case of rhodium, to larger cluster compounds such as the dinitride  $[\text{Rh}_{12}\text{HN}_2(\text{CO})_{23}]^{3-}$ ,<sup>2</sup> while in the case of cobalt only rearrangement of the metal framework to the octahedral  $[\text{Co}_6\text{N}(\text{CO})_{13}]^-$  was observed.<sup>3</sup> We have now investigated the pyrolysis of the cobalt species in more drastic conditions (diglyme,  $140^\circ\text{C}$ ) obtaining the new high nuclearity  $[\text{Co}_{14}\text{N}_3(\text{CO})_{28}]^{3-}$  anion, the first example of a trinitride cluster compound. The anion is shown in the Figure.



The unprecedented metal atom cluster consists of two superimposed rather folded centered-hexagons of cobalt atoms giving rise to a distorted fragment of simple hexagonal packing. Three alternate, out of the six, trigonal prismatic cavities are occupied by encapsulated nitrogen atoms. This situation resembles that present in binary phases of some metal carbides and nitrides. However the empty prisms are quite distorted. The CO ligands are disposed 12 edge bridging, and 14 terminally, one for each cobalt atom. The Co-Co bond lengths are rather scattered (range 2.42-2.94 Å).

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- 2) S. Martinengo, G. Ciani and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1986, 1742.
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REACTIONS OF  $[\text{Ir}_4(\text{CO})_{12}]$  and  $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})][\text{PPN}]$   
WITH MULTIDENTATE LIGANDS

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Following our discovery that the tripod ligand substituted iridium cluster  $[\text{Ir}_4(\text{CO})_9\{(\text{PPh}_2)_3\text{CH}\}]$  has an all-terminal CO ligand structure,<sup>1</sup> we have carried out further investigations into the reactions of  $[\text{Ir}_4(\text{CO})_{12}]$  and  $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})]^-$  with multidentate phosphine ligands.

The reactions to be described will include treatment of  $[\text{Ir}_4(\mu\text{-CO})_3(\text{CO})_8(\text{PPh}_3)]$  with  $\text{HC}(\text{PPh}_2)_3$  to give the all-terminal CO ligand cluster  $[\text{Ir}_4(\text{CO})_8(\text{PPh}_3)\{\text{HC}(\text{PPh}_2)_3\}]$ , and the reaction between  $[\text{Ir}_4(\text{CO})_{11}\text{X}]^-$  ( $\text{X} = \text{Br}, \text{SCN}$ ) and  $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ . In addition we report the crystal structure determination of an isomer of  $[\text{Ir}_4(\text{CO})_{11}(\text{SCN})]^-$ , which, as the  $\text{PPN}^+$  salt, contains three bridging CO ligands, in contrast to the recently reported<sup>2</sup> structure of the  $[\text{NBz}_2\text{Me}_2]^+$  salt which has an all-terminal CO ligand configuration.

1. J.A. Clucas, M.M. Harding, B.S. Nicholls, and A.K. Smith, J. Chem. Soc., Chem. Commun., 1984 319.
2. R. Della Pergola, L. Garlaschelli, S. Martinengo, F. Demartin, M. Manassero, and M. Sansoni, Gazz. Chim. Ital., 117, 245 (1987).

## SOME CHEMISTRY OF SULPHUR DIOXIDE SUBSTITUTED TRINUCLEAR PLATINUM CLUSTERS

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The ligand  $\text{SO}_2$  is comparable to CO both in its ability to stabilise clusters and their mutual labilisation by the addition of amine oxides. Recently routes into  $\text{SO}_2$  clusters in particular,  $[\text{Pt}_3(\mu\text{SO}_2)_3(\text{PR}_3)_3]$ , have been realised and the bonding and chemistry of these clusters explored.

We now report the systematic sequential substitution of CO into  $[\text{Pt}_3(\mu\text{SO}_2)_3(\text{PCy}_3)_3]$  which yields the mixed mono and bis substituted carbonyl clusters  $[\text{Pt}_3(\mu\text{SO}_2)_{3-n}(\mu\text{CO})_n(\text{PCy}_3)_3]$ , where  $n=1$  and 2 respectively. These compounds have been fully characterised by X-ray crystallography,  $^3\text{P}\{\text{H}\}$  and  $^{195}\text{Pt}\{\text{H}\}$  N.m.r., infra-red spectroscopy and microanalysis. Some correlation has been observed between the strength of the Pt—Pt bonds and the corresponding  $J_{\text{Pt-P}}$  coupling constant for the respective cluster. Also some mechanistic studies, primarily using I.R. stop flow techniques, have been undertaken to investigate the carbonylation of these clusters.

The labilisation of phosphines using isocyanide ligands on tri-platinum clusters has been further investigated using stoichiometric amounts of xylol isocyanide on the aforementioned mixed bridged clusters.

In addition the reaction of acetylides and terminal acetylenes have been investigated on both the mixed and homo bridged platinum clusters, where  $\text{Me}_3\text{NO}$  activation has been employed. For example, reaction of the 42-electron cluster  $[\text{Pt}_3(\text{SO}_2)_3(\text{PCy}_3)_3]$  with sodium acetylide has afforded the novel 44-electron cluster species  $[\text{Pt}_3(\text{SO}_2)_2(\mu\text{C}\equiv\text{CH})(\text{PCy}_3)_3]^-[(n\text{-Butyl})_4\text{N}]^+$  where the organic moiety bridges one edge of the platinum triangle through its  $\alpha$ -carbon. The reactivity of such organoclusters will be further discussed.

ANIONIC TRIMETALLIC COMPOUNDS WITH Fe-M-M' (M= Zn, Cd, Hg; M'= Fe, Mo, W )  
SKELETONS.

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As an extension of previous studies which have lead to the synthesis of neutral heterotrimetallic mercury compounds<sup>1</sup>, we have investigated the formation of anionic trimetallic compounds of zinc, cadmium and mercury.

The reaction of  $(\text{NET}_4)[\text{HFe}(\text{CO})_4]$  with  $\text{MX}_2$  (M= Zn, Cd, Hg; X= halides), produces the di-hydrides  $[(\text{OC})_4\text{HFe-Hg-FeH}(\text{CO})_4]$  which are sensitive towards  $\text{H}^+$  abstraction with BuLi to afford, with very good yields, the di-anions  $[(\text{OC})_4\text{Fe-M-Fe}(\text{CO})_4]^{2-}$ , stabilised as the  $\text{PPN}^+$  salts. Similar species have been prepared by different and longer routes<sup>2</sup>.

The complex  $(\text{PPN})_2[(\text{OC})_4\text{Fe-Hg-Fe}(\text{CO})_4]$  reacts with trimetallic  $[\text{Hg}\{\text{M}'(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$  (M'= Mo, W ) derivatives to give, after ligands redistribution, the new unsymmetrical  $(\text{PPN})[(\text{OC})_4\text{Fe-Hg-M}'(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$  (M'= Mo, W ) compounds.

The structural characterization of all these derivatives has been carried out by i.r. and n.m.r. spectroscopy. X-Ray crystal structure of the compound  $(\text{PPN})_2[(\text{OC})_4\text{Fe-Hg-Fe}(\text{CO})_4]$  is also reported.

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P.Braunstein, O.Rossell, M.Seco, I.Torra, X.Solans, and C.Miravittles, Organometallics, 1986, 5, 1113.
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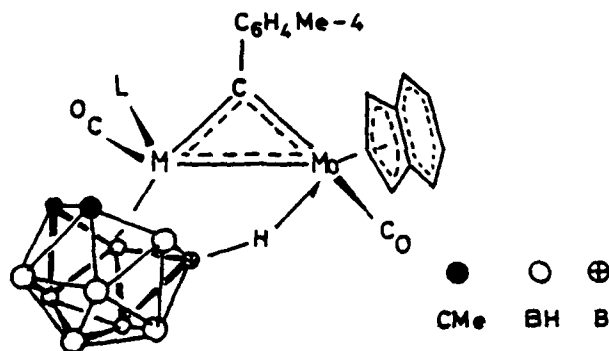
## SYNTHESIS AND REACTIVITY OF THE BIMETALLIC COMPOUNDS



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The anionic complexes  $[\text{M}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{L})(\eta^{n-4}\text{-C}_2\text{B}_n\text{H}_n\text{Me}_2)]^-$  ( $M = \text{Mo, W}$ ;  $n = 9, 10$ ;  $L = \text{CO, P(OMe)}_3$ ) react with the salt  $[\text{Mo}(\text{CO})_2(\text{NCMe})_2(\eta^5\text{-C}_9\text{H}_7)]^+[\text{BF}_4]^-$  to provide bimetallic compounds of the form  $[\text{MMo}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{L})(\mu\text{-H})(\eta^{n-4}\text{-C}_2\text{B}_n\text{H}_{n-1}\text{Me}_2)]$ :



The metal-metal bonds in these species are supported by bridging alkylidyne and borohydride groups. The non-innocence of these moieties will be discussed with reference to the reactions of these complexes with unsaturated organic substrates.

## LUMINESCENCE OF TUNGSTEN (0)-CARBYNE COMPLEXES

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Universidad de Chile, Casilla 653, Santiago-Chile.

Andreas Mayr and Donald S. Mc Clure, Department of Chemistry, Princeton University, Princeton, New Jersey 08544, U.S.A.

The emission spectra of some octahedral tungsten carbyne complexes of the type  $((W\equiv CAr) \times (CO)_{4-n}L_n)$  with monodentate and two bidentate ligands in solution of 2-methyltetrahydrofuran have been analyzed at 77 K and room temperature.

The observed luminescence in glass solution was completely depolarized when incident polarized light was used. The phenyl ring linked to the carbyne center was found as a fundamental structure for the new luminescent species, however substituents in this ring do not alter in a significant way the luminescent properties of it. The emission lifetime for these species at 77 K are in the range of biradical species (4 to 17  $\mu s$ ) in agreement with our model for a system of carbene nature as the luminescent chromophore excited state.

The emission of some octahedral single bidentate ligand tungsten carbyne complexes presents a nonsimple exponential decay according to time resolved spectroscopy data in the range of 1 to 60  $\mu s$ . These experimental data reveals a conformeric equilibrium in the ground and excited states derived from the bidentate ligand conformations.

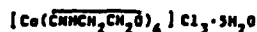
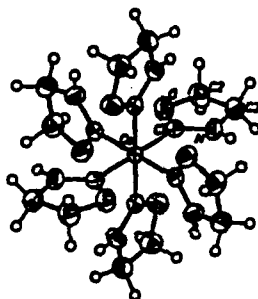
This work was supported by the Department of Energy and N.S.F. (Grants CHE 8506943 and CHE 8617472).

## New Homoleptic Carbene Complexes

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A series of oligo- and percarbene complexes has been synthesized from metal salts and 2-hydroxy isocyanides of which the hexacarbene complexes of cobalt(III) and rhodium(III) are most remarkable, e.g.<sup>1)</sup>



Both, their tendency of formation and stabilities are surprisingly high. By coupling of the carbene ligands in the coordination sphere of the metals, a further increase in stability of these complexes is to be expected. Several approaches to this aim will be reported including reactions of isocyanide complexes of palladium(II) and platinum(II) with diamines.

- 1) U. Plaia, H. Stolzenberg and W.P. Fehlhammer,  
J. Am. Ch. Soc. 107 (7), 2171 (1985)



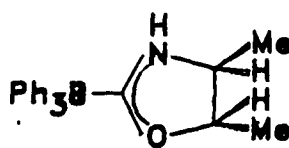
# Transition Metal and Boron Stabilized N,O-Carbenes: Similarities in Structure and Reactivity

H. Hoffmeister, B. Boyadjiev and W.P. Fehlhammer

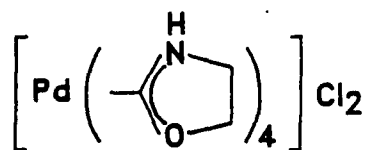
Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, D-1000 Berlin 33 (West-Germany)

Transition metal coordinated 2- and 3-hydroxyalkyl isocyanides spontaneously undergo intramolecular cyclization reactions to give hemoleptic carbene complexes [1, 2]. With triphenylboron, the same isocyanides give rise to (oxazolidin-2-ylidene)- and (perhydrooxazin-2-ylidene)triphenylboron [3].

The very similar effects of boron and transition metals on the stabilization of coordinated N,O-carbenes are established through X-ray analyses of (*trans*-4,5-dimethyloxazolidin-2-ylidene)triphenylboron 1 and, e.g., tetrakis(oxazolidin-2-ylidene)palladium(II)-dichloride 2 [1].



1



2

N-alkylation of the carbene ligands in both, transition metal and boron complexes is achieved on treatment with NaH and RI or  $[R_2O][BF_4]$  in dimethyl formamide.

The spectroscopic properties (ir, nmr, ms) of the compounds will be discussed.

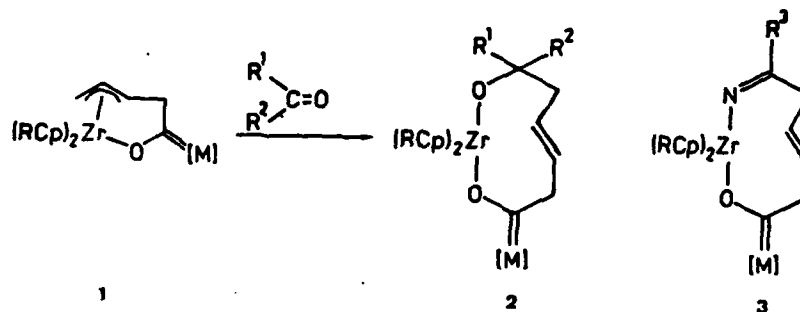
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 [2] Plaia, U.; Stolzenberg, H.; Fehlhammer, W.P. *J. Am. Chem. Soc.* 1985, 107, 2171.  
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Medium-sized Metallacyclic Carbene Complexes from  
(Butadiene)zirconocene, Metal Carbonyls and Organic Carbonyl  
Compounds

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Institut für Organische Chemie der Universität Würzburg  
Am Hubland, D-8700 Würzburg

Carbene complexes **1** are obtained by reacting metal carbonyls with the (butadiene)zirconocene reagent<sup>1)</sup>. Complexes **1** react with aldehydes, ketones or nitriles to give nine membered metallacycles **2** or **3**.



Complexes **2**, having a *trans*-configured C=C bond, exhibit a rather rigid chiral ring conformation. From the dynamic NMR spectra, Gibbs activation energies between 16 and 18 kcal/mol have been obtained for the topomerization process. The potential use of the metallacyclic carbene complexes in organic synthesis is discussed.

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A NEW SYNTHETIC ROUTE TO THE SECONDARY HETEROCARBENE COMPLEXES :  
 $[\text{Mo}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{PR}'_3)(\text{CHOR})]^+\text{X}^-$  ( $\text{R} = \text{H}, \text{Me}, \text{SiMe}_3$ )

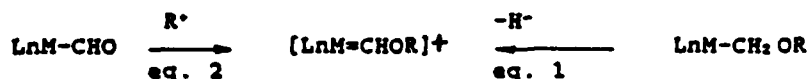
Ali Asdar, Véronique Guerschals, Claude Lapinte, Laboratoire de Chimie des Organométalliques, UA CNRS 415, Université de Rennes I, 35042 Rennes Cedex, France

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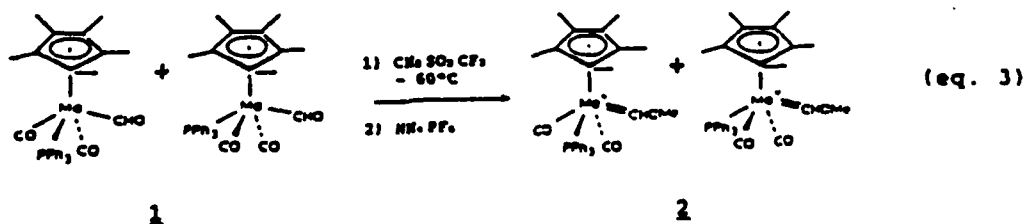
Few secondary cationic heterocarbene complexes ( $\text{LnM}^+=\text{CHOR}$ ) are known because their access are scarce.

Indeed, only the hydride abstraction reaction from metal alkyl compounds  $\text{LnM-CH}_2\text{OR}$  is operative (eq. 1). However, the hydride abstracting agents (the trityl cation and the methylene complex  $\text{LnM}^+=\text{CH}_2$ ) are either versatile or elusive.

Meanwhile the addition of electrophiles to the oxygen atom of the metal-acyl compounds is one of the main route to Fischer-type carbenes, up to now similar reactions from neutral metal formyl complexes have failed in synthesizing monocationic secondary heterocarbene compounds (eq. 2).



We have found that a cis-trans mixture of the new molybdenum formyl complex **1** reacts with electrophilic reagents like  $\text{H}^+$ ,  $\text{CH}_3^+$ ,  $\text{R}_3\text{Si}^+$  to yield the cis-trans mixture of the secondary metal-carbene in 60-80 % yield (eq. 3).



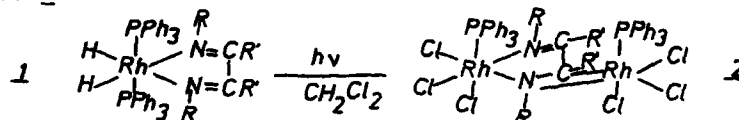
The X-ray crystal structure of **1** and the stereoselectivity of the reaction will be reported.

Photochemistry of  $[\text{RhH}_2(\text{R-DAB})(\text{PR}_3)_2]\text{PF}_6$  and their photoreactivity with acetylenes.

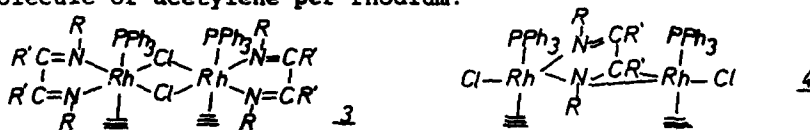
M. Iglesias, C. del Pino Instituto de Ciencia de Materiales, C.S.I.C. calle Serrano 113, 28006 MADRID, SPAIN.

A photochemical study of Rh(III) dihydrides,  $[\text{RhH}_2(\text{R-DAB})(\text{PR}_3)_2]\text{PF}_6$  1 (R-DAB = 1.4 diaza-1.3 butadiene) and their photochemical reactions with acetylenes in solution of  $\text{CH}_2\text{Cl}_2$ , acetone or THF has been made. The structures of the photoproducts appear to depend on the electronic properties of the ligands and the solvent used.

Reactions in  $\text{CH}_2\text{Cl}_2$ .— The starting product 1 after reductive elimination of  $\text{H}_2$ , loses a phosphine ligand, takes chlorine from the solvent by oxidative addition and the R-DAB ligand changes its coordination mode from  $\sigma, \sigma'$ -N, N' (4e) to  $\sigma$ -N,  $\mu^2$ -N',  $\eta^2$ -CN' (6e), 2.



The photochemical reaction with acetylenes gives 2 products: a pale yellow one with R-DAB ligand  $\sigma, \sigma$ -N, N', 4e coordinated, and Cl-bridged, in a very low yield 3 and product 4 with the ligand R-DAB  $\sigma$ -N,  $\mu^2$ -N',  $\eta^2$ -CN', 6e coordinated. In both cases there is one molecule of acetylene per rhodium.



Reactions with acetone and tetrahydrofuran.— The Rh(III) dihydrides with these solvents lose  $\text{H}_2$ , a phosphine ligand and R-DAB coordinates by 8e (acetone) or 6e (THF).

In their photochemical reactions with acetylenes the ratio  $\text{Rh}/\equiv = 1$  too.

As regards the photochemical mechanism, we are trying to find out from which excited state it occurs. Normally MLCT states are not reactivities. Reactions can however take place from a close-lying reactive state. The change of coordination mode of R-DAB ligands, has a great influence on the absorption spectra.

A complete study of U.V-Vis of these compounds has been done.

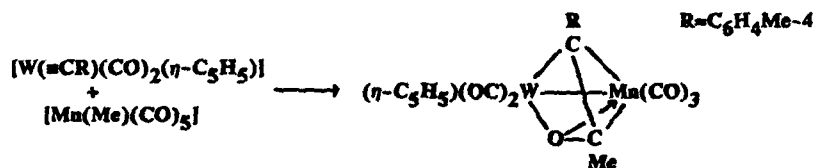
# **NOVEL ALKYLIDYNE ACYL COUPLING REACTIONS ON DINUCLEAR COMPLEXES**

L.J.Hart, J.C.Jeffery, R.M.Lowry and F.G.A.Stone

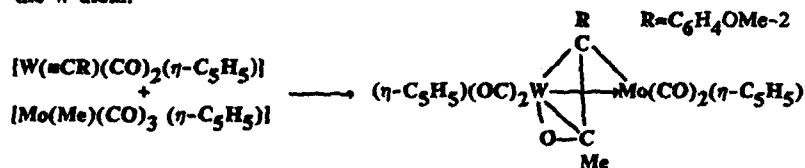
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The versatility of the compound  $[W(=CR)(CO)_2(\eta-C_5H_5)]$  ( $R=C_6H_4Me-4$ ) in rational stepwise cluster synthesis has long been established. However, reacting this complex with simple metal alkyl species has provided some surprising results.

The thermal reaction between  $[Mn(Me)(CO)_5]$  and  $[W(=CR)(CO)_2(\eta-C_5H_5)]$  yields the species  $[WMn(\mu-C(R)C(O)Me)(CO)_5(\eta-C_5H_5)]$ , whose structure has been established by X-ray crystallography. The study reveals the combination of the alkylidyne ligand and an acyl unit. The resulting  $C(R)(C(O)Me)$  bridging ligand has an acyl group that itself bridges the W-Mn bond, formally donating  $4e^-$  to the complex. The mechanism whereby the product is formed almost certainly involves the coordination of the  $W=CR$  triple bond to a transient  $[Mn(C(O)Me)(CO)_4]$  species. Carbon-carbon bond formation then takes place and CO is lost with coordination of the oxygen to the Mn atom.



In contrast, the photochemical reaction between the alkyl species  $[Mo(Me)(CO)_3(\eta-C_5H_5)]$  and  $[W(=CR)(CO)_2(\eta-C_5H_5)]$  ( $R=C_6H_4Me-4, C_6H_4OMe-2$ ) yields the  $[MoW(\mu-C(R)C(O)Me)(CO)_4(\eta-C_5H_5)_2]$ . The structure for  $R=C_6H_4OMe-2$  has been determined and reveals a completely different arrangement of the bridging  $C(R)C(O)Me$  ligand. In this complex the acyl  $C=O$  double bond acts as a  $2e^-$  donor to the W atom.



The structural and chemical properties of the new compounds will be discussed.

## HIGH-VALENT COMPLEXES OF ORGANOSULPHUR LIGANDS VIA

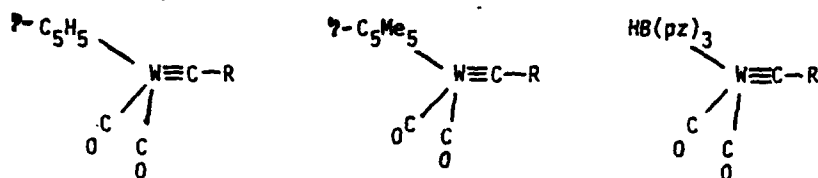
OXIDATIVE THIONYLATION OF  $[W(\eta\text{-C}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})_2(\text{L})]$  $(\text{L} = \eta\text{-C}_5\text{H}_5, \eta\text{-C}_5\text{Me}_5, \text{HB}(\text{pyrazol-1-yl})_3)$ 

Anthony E. Hill, Judith A.K. Howard, Nicholas H. Sanders and F. Gordon A. Stone

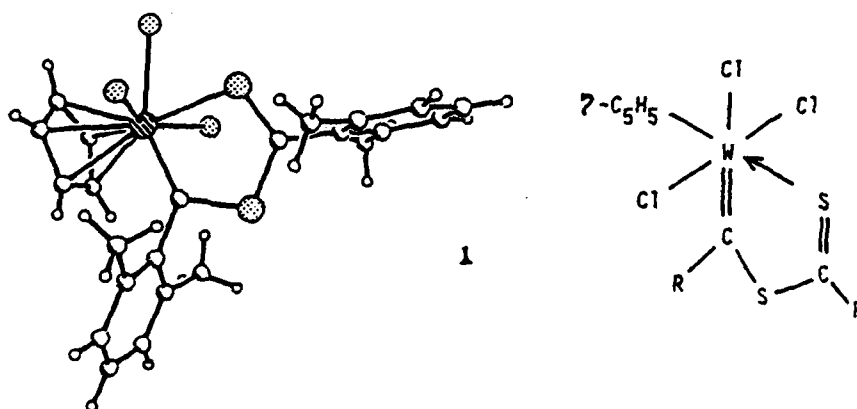
Department of Inorganic Chemistry, University of Bristol,  
Bristol BS8 1TS, Great Britain

An extensive coordination chemistry of carbon-bound organosulphur ligands ( $\text{CS}_2$ ,  $\text{C}(\text{S})\text{R}$ ,  $\text{=C}(\text{SR})_2$ ,  $\text{=C-SR}$  etc.) has developed, concerned primarily with low-valent, soft transition metal centres. In contrast, these types of ligands are rare in systems in which the metal is in a high oxidation state.

The alkylidynetungsten complexes

 $(\text{R} = \text{C}_6\text{H}_3\text{Me}_2\text{-2,6}, \text{pz} = \text{pyrazol-1-yl})$ 

react with thionyl chloride,  $\text{O}=\text{SCl}_2$ , providing access to a range of novel high-valent organosulphur complexes, of which **1** is an example. Mechanisms for the processes involved will be discussed in terms of the steric influence of the large  $\text{-C}_6\text{H}_3\text{Me}_2\text{-2,6}$  group, the degree of crowding at the tungsten centre, and the extent to which these effect the structures of the final products.



ORGANIC COMPOUNDS OF MERCURY, TIN AND LEAD AS INITIATORS OF  
VINYL MONOMER POLYMERIZATION

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Gorky, USSR

The goal-oriented search of new effective binary initiating systems based on homolytical reactions of organometallic compounds for polymerization and copolymerization of vinyl monomers (methyl methacrylate, acrylonitrile and others) has been performed:

1.  $R_nM$  and halides of transition (Ti, Mn, Ni, Fe, Co) and non-transition (Sn, Si) elements;
2.  $R_nMX$  and sodium borohydride or tetraphenylborate, where R is alkyl; M = Hg, Sn, Pb; X = Cl,  $CH_3COO$ .

The given systems have been found to initiate polymerization of the monomers mentioned at rather low temperature (20-50°C).

The following facts are indicative of free-radical mechanism of initiation: polymerization process is inhibited by hydroquinone additives, polymerization rate is directly proportional to square root of initiator concentration;  $K_g/K_t^{1/2}$  values, copolymer compositions are close to corresponding quantities for polymerization reaction on benzoyl peroxide.

The peculiarity of the initiating systems suggested is in the following: the polymerization process can be conducted in the presence of air oxygen, i.e. the latter does not inhibit and acts as a cocatalyst in some cases.

Polymers prepared on the initiating systems to use organic compounds of mercury, tin and lead, contain metal atoms in the composition of terminal groups; that is practically important for obtaining biologically resistant materials, block-copolymers and protective film-forming polymer coatings.

Dimethyldiethylaminoindium: a potential precursor for MOVPE technique.

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Metal Organic Chemical Vapor Epitaxy (MOVPE) is finding larger utilization as a method of preparing thin films of good quality for optoelectronic devices. However, several problems concerning C incorporation or parasitic pre-reactions are still limiting factors depending on the type of used precursors. Here we report on the synthesis of  $(Me_2InNEt_2)_2$  which shows promising chemical-physical properties for its use as a precursor in MOVPE. It can be obtained in good yield by two steps reaction of  $InCl_3$  and  $LiMe$  (1:2 molar ratio) and of the formed  $Me_2InCl$  with  $LiNEt_2$  (1:1 molar ratio) in diethyl ether solution as a colourless volatile solid (it melts at 55 C and readily sublimes at 40 C and  $10^{-2}$  Pa). It has been characterized by elemental analysis and IR and NMR spectroscopies; the mass spectrum suggests a dimeric structure. Almost complete prompt pyrolysis to metallic indium has been showed. Studies on gas-phase reactions with P or As donor molecules are in progress.



## AMORPHOUS GERMANIUM FROM VOLATILE HYDRIDES: INVESTIGATION ON REACTION MECHANISM

Mario Castiglioni, Giuseppe Cetini, Paola Michelin Lausarot, Lorenza Operti, Gian Angelo Vaglio, Mario Valle and Paolo Volpe, Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso M. d'Azeglio 48, I-10125 Torino, Italy.

Amorphous materials, which show semiconducting properties suitable for practical applications, can be obtained by thermal and  $\gamma$ -radiolytic decomposition of volatile organometallic and hydridic compounds. As the features of the solid material are strongly dependent on the experimental conditions, it is interesting to investigate the reactions of germanium hydrides in the gas phase, a relatively unexplored field (1). The gas phase behaviour of the ionic species originated from  $\text{GeH}_4$  has been studied by high pressure mass spectrometry. In self-condensation reactions,  $\text{GeH}_2^+$  appears to be the most reactive species, as it has already been suggested in processes involving radicals (2). Reactions of  $\text{GeH}_4$  with  $\text{O}_2$  give weak  $\text{GeH O}^+$  ( $n=0-3$ ) and  $\text{GeH O}_2^+$  ( $n=0-1$ ); with  $\text{NH}_3$  they give  $\text{GeNH}^+$  ( $n=2-6$ ); and with  $\text{CO}$  they give  $\text{GeH O}^+$  and  $\text{GeH C}^+$  ( $n=0-3$ ). The formation of these latter ions is likely to be due to the bridge coordination of a CO on the two germanium atoms of  $\text{Ge}_2\text{H}_n^+$  species. The relative abundances of the ionic products are affected by the total pressure and by the partial pressure ratio of the reagents.

Interesting results were obtained by investigating the amorphous material at different pressures. The composition of the solid product obtained at 1 atm pressure is  $\text{GeH}_{1.15}$  (2). Thermogravimetry and mass spectrometry analyses show that it loses a mixture of volatile germanes at 200 °C and monogermane at 875 °C, with a total weight loss of 23.4%. A sharp phase change is observed at 675 °C by DSC analysis and the X-ray spectra of the material, which is amorphous up to 675 °C, show the presence of two crystalline phases at higher temperature (3). Moreover, the solid shows EPR signals in the 600-700 °C range. Chemical properties, IR, MS and EPR spectra of the solid germanium hydride and of a carbon-germanium hydride will be discussed.

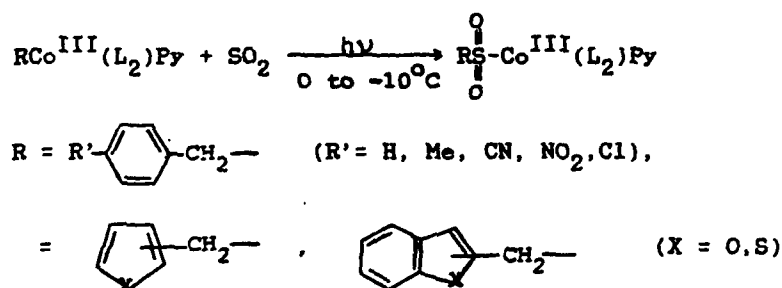
- 1 - J.K. Northrup and F.W. Lampe, J. Phys. Chem., 77, 30 (1973).
- 2 - R. Belluati, M. Castiglioni, P. Volpe and M.C. Gennaro, Polyhedron, 6, 441 (1987).
- 3 - P. Benzi, M. Castiglioni, P. Volpe, L. Battezzati and M. Venturi, Polyhedron, in press.

## Sulphur Dioxide Insertion into Co-C bond in Organocobaloximes

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Sulphur dioxide insertion into a metal-carbon bond takes place with a wide variety of sigma bonded organometallic complexes of both main groups and transition elements. Despite a great deal of work on the kinetics and stereochemistry of these reactions, no unified mechanism has emerged so far. We present an unambiguous experimental evidence that sulphur dioxide insertion reactions into benzyl, thienylmethyl and furylmethyl cobaloximes are not true insertions into Co-C bond. The products result as a consequence of intermolecular process in which organic and the metal fragments of the inserted products do not arise from the same organometallic substrate. The insertion occurs only under photochemical conditions and no inserted product is formed under thermal conditions.



L = dmgH (dimethylglyoxime mono anion)

= chgH (cyclohexaneglyoxime mono anion)

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3. A. Wojcicki, Adv. Organometal. Chem., 12, 31 (1974) and Ann. Acad. Sci. 239, 100 (1974).

## CO INSERTION IN METAL-CARBON BONDS IN THE IRON PORPHYRIN SERIES.

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Electrogenerated  $\text{Fe(I)}^-$  or  $\text{Fe(}^{100}\text{)}^{2-}$  porphyrins are known to react with alkyl halides (RX) leading to iron  $\sigma$  alkyl complexes (I) (1-3). The first study upon the reactivity of carbon monoxide towards such complexes under mild conditions is described (4).

The obtained results show that two different behaviors appear depending on the alkyl chain (R) nature. If  $\text{R} = -\text{CH}_3$  or  $-\text{C}_6\text{H}_5$  only complexation of I by CO takes place whereas CO insertion in the metal-carbon bond is effective, either for longer  $n$ -alkyl chains ( $-\text{C}_2\text{H}_5$  to  $\text{C}_8\text{H}_{17}$ ) or for ramified ones (secondary or tertiary), leading to the corresponding iron-acyl complexes. The spectral and electrochemical characteristics of the acyl compounds are determined for different iron porphyrins (octa- $\beta$ thyl, tetraphenyl, picket-fence or basket-handle). The mechanism of the insertion reaction is discussed. We can assume, according to the numerous literature concerning carbonyl complexes of transition metals, that the initial step consists in a  $\sigma$ -alkyl complex CO ligation followed by CO insertion. The kinetic of the latter step depends upon the oxidation state of the iron : the alkyl to acyl migration rate is enhanced by the electrochemical oxidation of the iron II species into the iron III one. The kinetic constants can be estimated using cyclic voltammetry.

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1. D. Lexa, J. Mispelter and J.M. Savéant. J.Am.Chem.Soc., 1981, 103, 6806.
2. D. Lexa, J.M.Savéant and D.L. Wang. Organometallics, 1986, 5, 1428.
3. C. Gueutin, D. Lexa, J.M.Savéant and D.L. Wang .Submitted
4. C. Gueutin, D.Lexa and J.M. Savéant. Submitted.

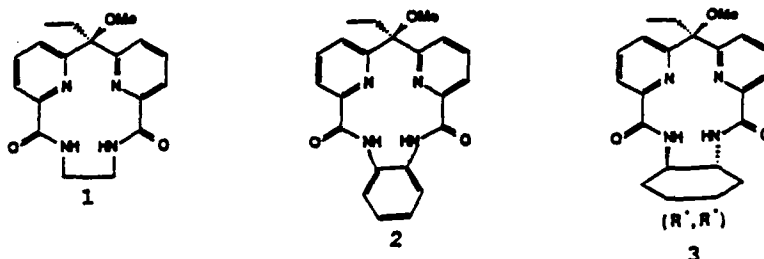
**METAL COMPLEXES OF MACROCYCLES FROM  
DIPYRIDYLMETHANE-DIAMINE DERIVATIVES FOR POTENTIAL  
CATALYTIC APPLICATIONS**

Christina Moberg and Kenneth Wärnmark

Department of Organic Chemistry, Royal Institute of  
Technology, S-100 44 STOCKHOLM, Sweden.

Chiral synthetic macrocyclic compounds capable of coordination to transition metal ions are attractive for use in selective synthetic transformations. By proper design, the macrocyclic ligand should be able to choose the desired substrate and direct the substrate in a regio- and stereospecific fashion towards the metal center.

We have been able to synthesize macrocyclic ligands from dipyridylmethane derivatives and diamines, e.g 1 and 2. Use of the chiral diamine R,R-trans-1,2-diaminocyclohexane gives the chiral macrocyclic ligand 3 in high yield. According to NMR-data 3 has a rigid conformation with two different amide-protons.



The ligands form complexes with transition metal ions like  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$ . According to spectroscopic data,  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$  have square planar coordination to 3.

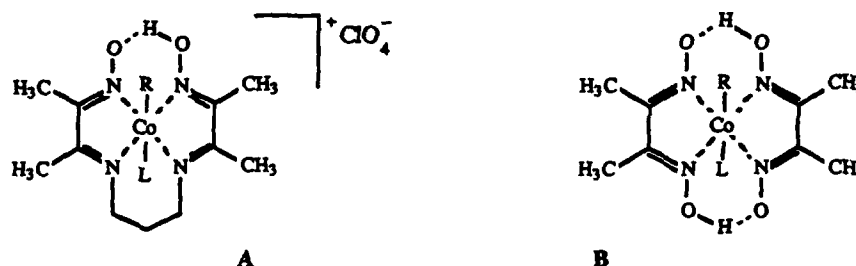
Metal-pyridyl ligands are good catalysts in oxidative transformations. The usefulness of our macrocyclic ligands in such processes will be investigated.

## $^{59}\text{Co}$ NMR OF VITAMIN B<sub>12</sub> MODEL COMPOUNDS

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 b) Dipartimento di Scienze Chimiche, Università di Trieste, I-34127 Trieste (Italy)

Because of the biochemical importance of the Cobalt-Carbon bond in cobalamines and other experimental studies on the nature of this bond<sup>1)</sup> a large number of Vitamin B<sub>12</sub> model compounds of type A and type B (cobaloximes) have been investigated by  $^{59}\text{Co}$  NMR. Whereas the Co chemical shift is strongly dependent on the nature of the axial and equatorial donor ligands, a less pronounced but significant dependence on the structure of the axial carbon ligand is observed.



Our results show that

- a) changing of the equatorial ligand causes a chemical shift of about 500 ppm, cobaloximes appearing at lower frequencies than type A compounds.
- b) variation of the coordinating axial donor ligand L results in a chemical shift dispersion, depending upon the structure of R, e.g.  $\Delta\delta$  (aquo/pyridine) in benzyl-compounds is 645 ppm, compared with 380 ppm in acetyl-compounds.
- c) in the series of alkyl-cobaloximes (methyl, ethyl, n-propyl, n-butyl, isopropyl, benzyl), the trend in the  $^{59}\text{Co}$  chemical shifts is rather complex. Increased shielding is found in going from methyl to ethyl (30-100 ppm), thus reflecting an inductive effect. In all other alkyl compounds, a deshielding is observed (up to 460 ppm) with increasing chain length or branching, most pronounced in benzyl and isopropyl complexes (steric effect).
- d) variation of the Co-C bond length in cobaloximes is reflected in the  $^{59}\text{Co}$  chemical shift. This is in agreement with an EHMO study<sup>2)</sup> which predicts a smaller HOMO-LUMO gap with increasing Co-C bond distance. The expected deshielding effect is indeed observed.

1) J. Halpern, *Science* 227, 869 (1985); G. Costa et al., *Gazz. Chim. Ital.* 116, 735 (1986)

2) C. Mealli, M. Sabat, L. G. Marzilli, *J. Am. Chem. Soc.* 109, 1593 (1987)

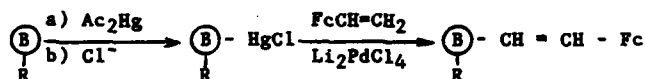
## FIRST EXAMPLES OF "METALLOCENONUCLEOSIDES"

Philippe Meunier, Issa Ouattara, Bernard Gautheron, Jean Tirouflet and  
Jack Besançon

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS  
(UA 33), Faculté des Sciences, 6 bd Gabriel 21000 Dijon (France)

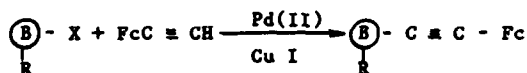
First examples of ferrocenyl substituted pyrimidine and purine nucleosides  
have been synthesised according to the following sequences :

## 1) Reaction of vinylferrocene on a 5-chloromercuri nucleoside



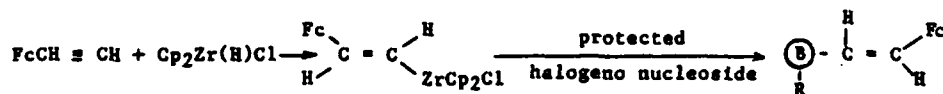
R = CH<sub>3</sub>, sugar      Fc = ferrocenyl      B = bases : pyrimidines

## 2) Halogenonucleoside and ethynylferrocene coupling



R = H, sugar      B = bases : purines, pyrimidines

## 3) Hydrozirconation reaction



R = sugar      B = bases : purines, pyrimidines

The whole of the compounds were characterized by <sup>1</sup>H NMR and mass spectrometry.

Cytotoxic properties of metallocenonucleosides have been tested "in vitro" on L 1210.

REACTIVITY OF METALLOCENES IN REACTIONS WITH  
ORGANOCADMIUM COMPOUNDS

G.A.Razuvaev, V.P.Mar'in, L.I.Vyshinskaya (Institute of  
Chemistry, Academy of Science, Gorky, U.S.S.R.)

Reactions of the  $\text{Cp}_2\text{M}$  metallocenes ( $\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Co}, \text{Fe}, \text{Ni}$ ) with  $\text{R}_2\text{Cd}$  have been discussed. It has been found that the reactivity of metallocenes depends on the nature of the central atom and in a number of cases by the R groups.

When  $\text{Cp}_2\text{V}$  ( $\text{Cp} = \text{C}_5\text{H}_5, \text{C}_5\text{H}_4\text{Alk}, \text{C}_5\text{Me}_5$ ) interacts with  $\text{R}_2\text{Cd}$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}$ ) the bielectronic oxidative addition to vanadocene take place to form  $\text{Cp}_2\text{VR}_2$ . At the same time the reaction of  $\text{Cp}_2\text{V}$  with  $\text{R}_2\text{Cd}$  ( $\text{R} = \text{Ph}, \text{GeEt}_3$ ) results in  $\text{Cp}_2\text{VR}$ .

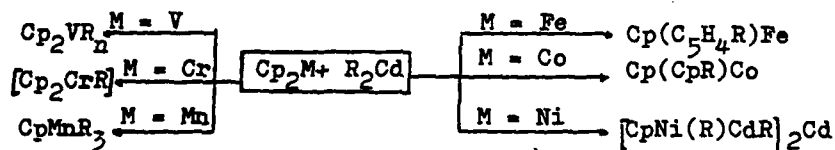
The oxidative addition of  $\text{R}_2\text{Cd}$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Ph}$ ) to  $\text{Cp}_2\text{Cr}$  occurs through sandwich-covalent chromium derivatives the existence of which have been confirmed by their conversion products and also by the low-temperature IR spectroscopy.

By the reaction of  $\text{Cp}_2\text{Mn}$  ( $\text{Cp} = \text{C}_5\text{H}_5, \text{C}_5\text{H}_4\text{Alk}$ ) with  $\text{R}_2\text{Cd}$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$ ) the  $\text{CpMnR}_3$  compounds have been obtained. In the reaction unstable intermediate has been registered by low-temperature IR spectroscopy method.

Ferrocene reacts with  $\text{R}_2\text{Cd}$  ( $\text{R} = \text{Alk}$ ) to form the homolytic substitution products under thermal decomposition conditions of organocadmium compounds.

Cobaltocene reaction with  $\text{R}_2\text{Cd}$  ( $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{CH}_2\text{SiMe}_3, \text{GeEt}_3, \text{Ph}$ ) results to homolytic addition product such as  $(\eta^5\text{-Cp})(\eta^4\text{-CpR})\text{Co}$ .

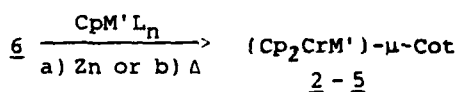
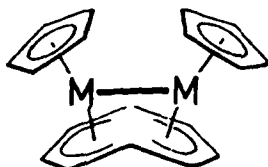
Nickelocene reacts with organocadmium compounds to form the polynuclear complex with Ni-Cd bond.



SYNFACIAL HOMO- AND HETEROBINUCLEAR CYCLOOCTATETRAENE COMPLEXES  
(CpM)<sub>2</sub>-μ-Cot: TOWARDS A NEW CLASS OF COMPOUNDS

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Fachbereich Chemie der Philipps-Universität, Hans Meerwein-Straße,  
D-3550 Marburg, FRG

The preparation of the synfacial homobinuclear Cot-complexes (CpM)<sub>2</sub>-μ-Cot (M = V, Cr) was first achieved by a one-pot-reaction of MCl<sub>2</sub>, K<sub>2</sub>Cot, and NaCp.<sup>1,2</sup> For the synthesis of the corresponding heterobinuclear complexes (Cp<sub>2</sub>MM')-μ-Cot the sandwich compound (η<sup>5</sup>-Cp)Cr(η<sup>6</sup>-Cot)<sub>2</sub> (6) can be employed as a valuable precursor (1).



M = V (1)  
M = Cr (2)

a) M' = V, L<sub>n</sub> = Cl<sub>2</sub> → 3  
a) M' = Cr, L<sub>n</sub> = Cl<sub>2</sub> → 2  
b) M' = Fe, L<sub>n</sub> = C<sub>6</sub>H<sub>6</sub> → 4  
b) M' = Co, L<sub>n</sub> = (C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> → 5 (1)

Because of chemical and structural results the addition of a second CpM-unit exclusively occurs synfacially to the CpCr-moiety. As the only diamagnetic compound the dichromium complex 2 can be identified. The divanadium species on the other hand has an excited triplet state, which can be populated thermally as proved by <sup>1</sup>H-NMR spectroscopy. NMR-measurements indicate two unpaired electrons for 4. ESR spectroscopically a localization of the unpaired electron in 3 and 5 can be observed on the less noble metal centre.

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- 2) Ch. Elschenbroich, J. Heck, W. Massa und R. Schmidt, Angew. Chem. 95 (1983) 319
- 3) J. Müller und H. Menig, J. Organomet. Chem. 96 (1975) 83;  
J. Heck und G. Rist, J. Organomet. Chem. 342 (1988) 45

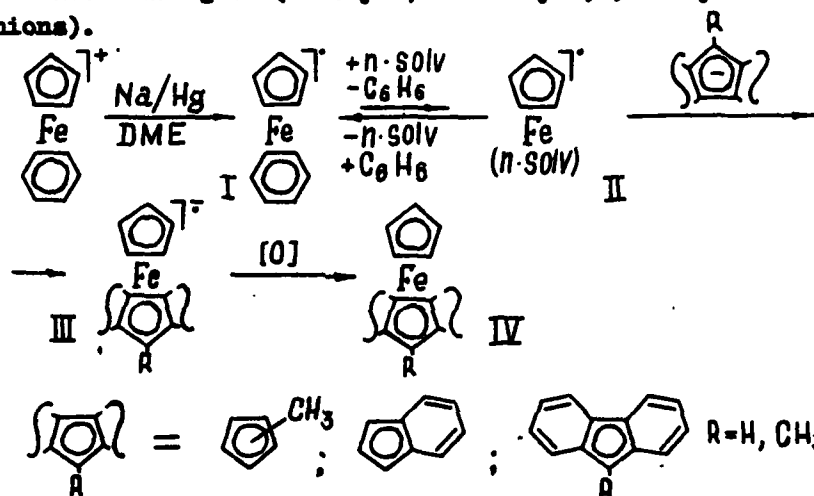


THE ANION-RADICAL SYNTHESIS OF UNSYMMETRICAL  
IRON SANDWICH COMPLEXES

L.N.Novikova, N.A.Pomazanova, N.A.Ustynyuk, D.N.Kravtsov

Institute of Organoelement Compounds, USSR Academy of Sciences,  
28 Vavilov str., Moscow, 117813, USSR.

The methodology of radical nucleophilic substitution[1] has been employed for synthesis of iron unsymmetrical sandwich complexes. The neutral 19-electron complex I easily exchanges the benzene ligand for methylcyclopentadienyl-anion and its condensed analogues (indenyl-, fluorenyl-, 9-methylfluorenyl-anions).



The key step of the whole process is the interaction of the anion with radical II, leading to anion-radicals III. The mild oxidation of III at the final step gives the corresponding neutral complexes IV. [2].

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2. N.A.Ustynyuk, N.A.Pomazanova, L.N.Novikova, D.N.Kravtsov, Yu.A.Ustynyuk, *Izvestiya Akademii Nauk, seriya Khimicheskaya*, **1986**, p.1688.

Reactivity of the Protonated "Open Ruthenocene" Salt  $[\text{Ru}(\eta^5\text{-C}_7\text{H}_{11})_2\text{H}] \text{BF}_4$

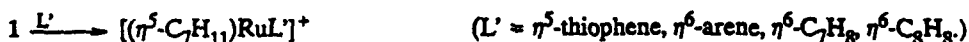
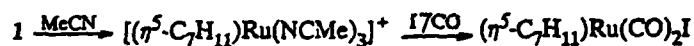
David N. Cox, Tito Lumini and Raymond Roulet.

Institut de Chimie Minérale et Analytique de l'Université

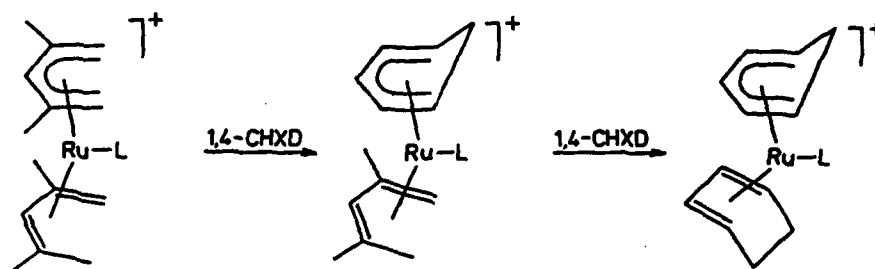
3, Place du Château, CH-1005 Lausanne, Switzerland.

As part of a general study of the chemistry of octadienediyl ruthenium complexes, the title compound, **1**, has been prepared in good yield by treatment of the octadienediyl ruthenium (IV) dichloride dimer,  $[(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\text{RuCl}_2]_2$ , with  $\text{AgBF}_4$  and 2,4-dimethylpentadiene.<sup>1</sup>

A wide range of monopentadienyl ruthenium derivatives are accessible from **1**:



Whereas the reactions of complexes **2a** to **2c** with 1,3-cyclohexadiene yield the cations  $[(\eta^5\text{-C}_7\text{H}_{11})\text{Ru}(\eta^4\text{-C}_6\text{H}_8)\text{L}]^+$  by simple displacement of the 2,4-dimethylpentadiene ligand, the reactions of complexes **2a** and **2b** with 1,4-cyclohexadiene proceed as shown below:



Further reactivity of **1** will also be discussed.

1. D.N.Cox and R.Roulet, JCS Chem. Commun. in press.

VIBRATIONAL SPECTRA OF TRIPLE-DECKER SANDWICHES OF RUTHENIUM  
AND OSMIUM WITH CENTRAL PENTAMETHYLCYCLOPENTADIENYL LIGAND

I.A.GARBUZOVA, A.R.KUDINOV, S.S.BUKALOV, M.I.RYBINSKAYA,  
B.V.LOKSHIN

A.N.Nesmeyanov Institute of Organoelement Compounds of the USSR  
Academy of Sciences, Vavilov st. 28, 117813 Moscow (USSR).

The triple-decker complexes of ruthenium and osmium  
( $\eta$ -C<sub>5</sub>R<sub>5</sub>)M( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)M'( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)PF<sub>6</sub> (M=M'=Ru, R=H, Me; M=Ru, M'=Os, R=H), containing 30 valence electrons, are studied by the methods of Raman and Infrared spectroscopies. The assignment is proposed by comparison with the spectra of corresponding metallocenes and its cations. The normal coordinate analysis of the C<sub>5</sub>Me<sub>5</sub>-ligand is also carried out using the force field of C<sub>5</sub>H<sub>5</sub>-anion /1/.

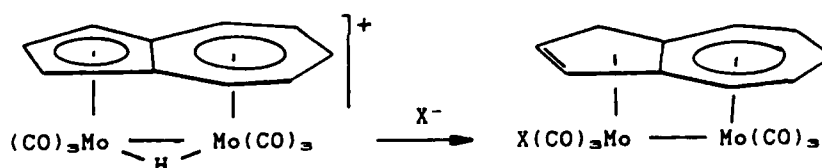
Resonance Raman enhancement have been observed for symmetric ring-metal stretching vibrations at 140-160cm<sup>-1</sup> and 370-380cm<sup>-1</sup>, for the out-of-plane C-Me deformation mode at 440cm<sup>-1</sup> and for the ring-breathing mode of C<sub>5</sub>H<sub>5</sub>-ring at 1102cm<sup>-1</sup>. The bands of methyl groups vibrations and the bands of very coupled ring-breathing and C-Me stretching modes of C<sub>5</sub>Me<sub>5</sub>-ring at 1428 and 590cm<sup>-1</sup>, very intensive in the Raman spectra of decamethylmetallocenes, became relatively weak in the Raman spectra of triple-decker sandwiches. The methyl groups vibration bands of central and terminal rings coincide, while the methyl group signals of the central and terminal rings in <sup>13</sup>C - <sup>1</sup>H NMR spectra are distinguished. The frequencies of symmetric ring-metal stretching modes at 140-170cm<sup>-1</sup> in the spectra of triple-decker sandwiches and decamethylmetallocenes increase upon transition from Ru to Os in accordance with the strengthening of metal-ring bond.

1 -I.A.Garbusova, O.G.Garkusha, B.V.Lokshin, J.Mink, Izv. Acad. Nauk SSSR, Ser. Khim., 8 (1988)

THE CHEMISTRY OF POLYAROMATIC-POLYMETALLIC COMPLEXES OF THE  
GROUP VI METALS

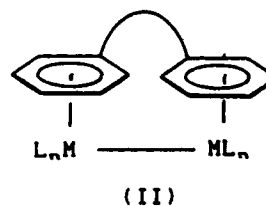
Kirsten E. Clode and Anthony H. Wright, Chemistry Department,  
University of Nottingham, Nottingham, NG7 2RD, U.K.

Polyaromatic-polymetallic complexes containing both fused and tied aromatic ligands are being investigated. The results of photochemical and electrochemical studies will be described. With systems containing fused polyaromatic rings (I), unexpected metal-ligand hydrogen migration reactions have been observed:



Two dimensional NMR and deuteration studies have revealed that these migration reactions are both stereospecific and regiospecific. Photochemical substitution reactions are likewise regiospecific.

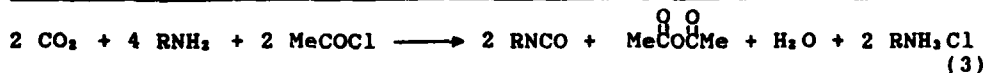
In polyaromatic systems containing rings tied by a saturated hydrocarbon link (II), photochemical activation has been used to generate new complexes containing metal-metal bonds. The electrochemical properties and chemical reactivity of these complexes will be described.



## METAL-ASSISTED INCORPORATION AND DEOXYGENATION OF CARBON DIOXIDE

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Incorporation of carbon dioxide into organic substrates, with formation of C-CO<sub>2</sub>, O-CO<sub>2</sub>, or N-CO<sub>2</sub> bonds, is an interesting subject.<sup>1</sup> Prior coordination of carbon dioxide to a metal cation as the *N,N*-dialkylcarbamato group, [M(O<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>]<sub>n</sub>,<sup>2</sup> may accomplish the twofold objective of stabilizing carbon dioxide as an O-donor and promote its reactivity towards electrophiles.<sup>3</sup> We have now found that metal *N*-alkylcarbamato complexes react easily with acyl halides, and alkyl isocyanates are chiefly formed. The overall process (equation 1-3), operating at room temperature and atmospheric pressure, corresponds to the metal-assisted deoxygenation of carbon dioxide, and to the direct synthesis of alkylisocyanates from primary amines.



M = Mn, Co; R = *n*-Pr, Cy

Both kinetic and thermodynamic factors concur favourably to the formation of isocyanate, and the proposed mechanism shows that the metal plays an important role in both these aspects.

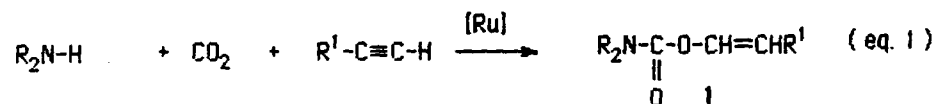
- 1) S. Inoue, N. Yamazaki, *Organic and Bioorganic Chemistry of Carbon Dioxide*, Kodansha, Tokyo, 1982.
- 2) D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, G. Pelizzi, *Chem. Ber.*, 1987, 120, 955.
- 3) D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, *J. Chem. Soc. Chem. Commun.*, 1986, 1000.

ONE-STEP CATALYTIC SYNTHESIS OF CARBAMATES FROM ALKYNES AND CO<sub>2</sub>

Christian Bruneau and Jean Fournier

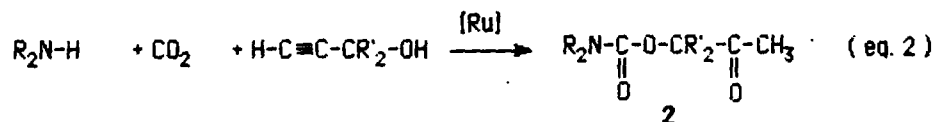
Laboratoire de Chimie de Coordination Organique, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex (France).

Alkynes can be activated towards nucleophiles in the presence of ruthenium complexes. Enol carbamates have been synthesised by catalytic addition of secondary amines and CO<sub>2</sub> to terminal alkynes such as phenylacetylene or 1-hexyne. (eq.1). Ruthenium complexes such as (C<sub>6</sub>Me<sub>6</sub>)RuCl<sub>2</sub>PR<sub>3</sub> and RuCl<sub>2</sub>(pyridine)(norbornadiene) are especially efficient catalysts. The reaction is highly regioselective and leads to the addition of the carbamate at the unsubstituted carbon of the alkyne (1).



This synthesis can be extended to the formation of vinylcarbamates, transparent polymer precursors, directly from acetylene itself with selective catalysts.

Propargylic alcohols react differently with secondary amines and actually afford β-oxoalkylcarbamates (2). The reaction is not possible with primary amines. However, the corresponding β-oxoalkylcarbamates can be obtained by addition of primary amines to the propargylic alcohol cyclic carbonate which is a possible intermediate in the catalytic reaction (eq.2).



NOVEL REACTIONS OF ALKYNES WITH  $\eta^2\text{CS}_2$  METAL COMPLEXES.

Françoise Conan, Jean Sala-Pala, Jacques-E. Guerschais.

Université de Bretagne Occidentale, UA CNRS 322 "Chimie, Electrochimie et Photochimie moléculaires", Faculté des Sciences et Techniques, Laboratoire de Chimie Inorganique Moléculaire, 6 avenue Le Gorgeu, 29287 BREST-FRANCE -

The utilization of carbon disulphide in transition metal-mediated reactions of organic molecules is an important problem. One of the most fruitful current areas of research is that in which alkynes react with coordinated  $\text{CS}_2$ . We describe reactions of alkynes with the  $\text{CS}_2$  complex  $[\text{Mo}(\text{CS}_2)(\eta\text{-C}_5\text{H}_5)_2]$ , and the structural characterization of three unprecedented types of  $\text{CS}_2$ -alkyne combination, involving one, two or three molecules of alkyne.

A. The addition of *one* molecule of alkyne to coordinated  $\text{CS}_2$  has been previously observed to occur either across the two sulphur atoms, giving a carbene ligand, or across the metal and a sulphur atom, giving a metallacycle  $\text{MC}(\text{S})\text{SC}(\text{R})\text{C}(\text{R})$ . We describe alkyne addition across the metal and the carbon atom of  $\text{CS}_2$  to give a metallacycle  $\text{MSC}(\text{S})\text{C}(\text{R})\text{C}(\text{R})$ .

B. Recently it has been reported that reactions of alkynes with coordinated  $\text{CS}_2$  can give complexes in which *two* molecules of alkyne are combined with  $\text{CS}_2$ . We display a new type of combination of  $\text{CS}_2$  with two alkynes, in which the cyclopentadienyl ligand intervenes.

C. Finally, we report the first example of a complex in which coordinated  $\text{CS}_2$  is combined with *three* molecules of alkyne.

I. TRANSITION-METAL-CATALYSED REACTIONS OF DIAZOESTERS :  
 INSERTION INTO C-H BONDS OF PARAFFINS BY CARBENOIDS

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<sup>a</sup> *Laboratory of Macromolecular Chemistry and Organic Catalysis,*

<sup>b</sup> *Laboratory of Organic Synthesis and Catalysis,*  
*University of Liège, Sart-Tilman (B.6), B-4000 Liège, Belgium*

When compared to transition-metal-mediated carbene transfer to unsaturated substrates, the direct "insertion" into C-H bonds of alkanes generally suffers from low yields and lack of selectivity. In principle such drawbacks should be overcome by stabilizing carbene species by coordination to suitable metal complexes. Moreover, in order to achieve efficient reactivity towards paraffins, the catalyst should be stable towards intramolecular carbene reactions (so as to suffer minimum deactivation) while the reactivity of the complexed carbene should permit insertion into non-activated C-H bonds.

Accordingly, it appeared that some electron-poor rhodium derivatives catalysed the decomposition of diazoesters at room temperature and promoted the reactions of the so-generated carbonylcarbenes (or carbenoids) with alkanes <sup>\*</sup>. High yields in ester functionalized molecules were obtained with cycloalkanes. Linear branched paraffins gave somewhat poorer results. However, temperature dependence of the yields were considerable, as well as dilution effects (ratio substrate to diazoester) and size of the diazoester alkoxy-group.

These results led us to study in detail the catalytic addition of carbenes, generated from diazoacetates, to saturated hydrocarbons, and to try to understand the following facts :

- unexpected regioselectivities,
- competitive experiments between pairs of alkanes,
- addition of radical traps and of carbon tetrachloride,
- deuterium isotope effects, ...

This communication will be a summary of our studies of the mechanistic aspects of this reaction and provide a working hypothesis for the future.

<sup>\*</sup> (a) N. Petiniot, A.F. Noels, A.J. Anciaux, A.J. Hubert, and Ph. Teyssié, "Fundamental Research in Homogeneous Catalysis", Plenum Press, New York and London, 1979, Vol. 3, p. 421; (b) A. Demonceau, A.F. Noels, A.J. Hubert, and Ph. Teyssié, *J. Chem. Soc., Chem. Commun.*, 688 (1981); (c) *Bull. Soc. Chim. Belg.*, 93, 945 (1984).



## II. ON THE EFFECTS OF WEAK INTERACTIONS ON THE SELECTIVITIES IN REACTIONS OF RHODIUM CARBENOIDS WITH ALKANES

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University of Liège, Sart-Tilman (B.6), B-4000 Liège, Belgium

Rhodium(II) carboxylates are very efficient catalysts for promoting, under mild conditions, the insertion of carbenes (generated from diazoacetates) into the C-H bonds of alkanes.

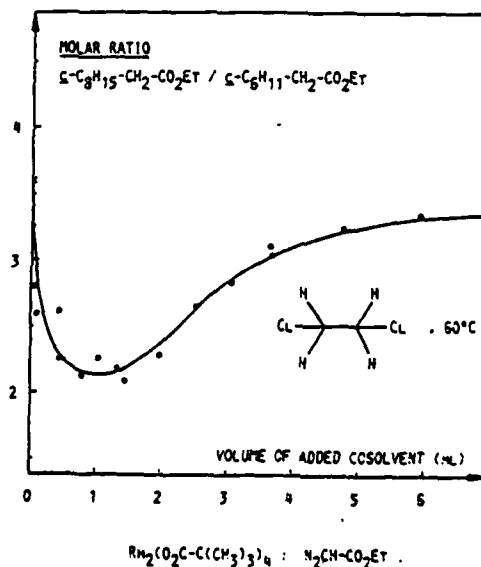
The selectivity of insertion strongly depends on both the diazoacetate alkoxy-group and the metal counter-ion.

Moreover, we have observed recently that the relative reactivities between cycloalkanes depend also on the presence of "inert" cosolvent as well as, surprisingly enough, on the amount of added cosolvent (Figure).

These unexpected influences of the catalyst and diazoester substitution on the selectivities, together with preferential reactions in competitive experiments between pairs of alkanes pointed out the importance of "solvation effects", even with paraffins. The formation of preferred "carbenoid-substrate" solvates was therefore postulated to rationalize the observed chemoselectivities in competitive experiments.

### INTERMOLECULAR COMPETITIONS BETWEEN CYCLOOCTANE AND CYCLOHEXANE

INFLUENCE OF ADDED 1,2-DICHLOROETHANE



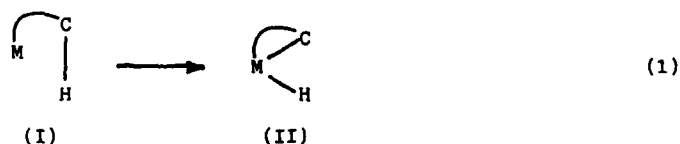
A. Demonceau, A.F. Noels, and A.J. Hubert, submitted for publication.

INTRAMOLECULAR C-H OXIDATIVE ADDITION AT IRIDIUM . SYNTHESIS AND CHARACTERIZATION OF  $[\text{Ir}(\text{H})(\text{CO})(\text{bq})\text{L}_2]\text{PF}_6$  (bq = 7,8-benzoquinolinato).

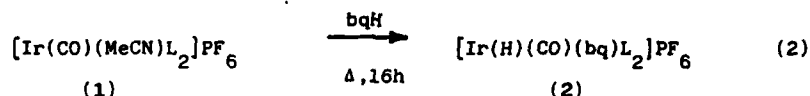
Mauro Ghedini , Francesco Neve , Dipartimento di Chimica , Università della Calabria, I-87030 Arcavacata di Rende (CS), Italy

Antonio Tiripicchio and Franco Ugozzoli, Istituti di Chimica Generale ed Inorganica e di Strutturistica Chimica , Università di Parma , Viale delle Scienze, I-43100 Parma, Italy.

Thermal activation of a C-H bond is the most common way to obtain cyclometallated complexes.<sup>1</sup> On the other hand oxidative addition to give the hydride derivative (II) (eq. 1) is relatively uncommon.



We now report the formation of  $[\text{Ir}(\text{H})(\text{CO})(\text{bq})\text{L}_2]\text{PF}_6$  (2) ( $\text{L} = \text{PPh}_3$ ) , achieved in good yield by reaction of  $[\text{Ir}(\text{CO})(\text{MeCN})\text{L}_2]\text{PF}_6$  with benzo[h]quinoline (bqH) (eq. 2) .



The spectroscopic data for 2 [ $\text{IR}$ ,  $^1\text{H}$  NMR and  $^{31}\text{P}$ -{selective  $^1\text{H}$ } NMR ] account for an hydride group trans to the nitrogen of the cyclometallated bq and two mutually trans  $\text{PPh}_3$  groups. The metallated carbon atom appears as a triplet in the  $^{13}\text{C}$ -( $^1\text{H}$ ) NMR spectrum. On this basis we assume the structure of 2 similar to that of the known aquo complex  $[\text{Ir}(\text{H})(\text{H}_2\text{O})(\text{bq})\text{L}_2]\text{SbF}_6$ .<sup>2</sup> The determination of the crystal structure of 2 by X-ray diffraction methods is in progress .

Reactivity of 1 with different BH ligands [e.g. 8-methylquinoline (mqH) and 2-phenylpyridine (ppyH)] is currently under investigation.

- 1 - E.C.Constable, Polyhedron, 3, 1037 (1984); G.R.Newkome et al., Chem.Rev., 86, 451 (1986).
- 2 - R.H.Crabtree and M.Lavin, J.Chem.Soc.,Chem.Comm., 794 (1985); R.H.Crabtree, personal communication ,1988.

## OXIDATIVE ADDITION/REDUCTIVE ELIMINATION OF ALDEHYDES AND KETONES AT RHODIUM.

Claudio Bianchini, Andrea Meli, Maurizio Peruzzini, Josè Antonio Ramirez, Alberto Vacca, Francesco Vizza and Fabrizio Zanobini, Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., Via J. Nardi; 39, I-50132 Firenze, Italy.

A great deal of research is presently focused to the synthesis and characterization of hydrido acyl complexes, because of their primary role in various rhodium catalyzed processes involving aldehydes.

In the course of our studies on the activation of C-H and H-H bonds at rhodium and iridium fragments with the tripodal ligands  $N(CH_2CH_2PPh_2)_3$ ,  $NP_3$ , and  $P(CH_2CH_2PPh_2)_3$ ,  $PP_3$ , we have found that the electronically and coordinatively unsaturated systems  $(NP_3)Rh^+$  and  $(PP_3)Rh^+$  are highly effective in the cleavage of C-H bonds from saturated and unsaturated hydrocarbons.<sup>1</sup> Herein we report on the reactions of aldehydes with the  $NP_3$  and  $PP_3Rh$  systems.

The  $(PP_3)Rh^+$  fragment is unable to keep in mutual cis disposition hydride (or alkyl) and acyl ligands, invariably promoting the reductive elimination of aldehydes (or ketones). By contrast the isoelectronic  $(NP_3)Rh^+$  fragment easily inserts across the formyl C-H bond from different aldehydes to yield quite robust octahedral cis-hydrido(acyl) complexes of rhodium (III). These have been fully characterized by chemical physical measurements and NMR spectroscopic techniques.

References: (1) C. Bianchini, A. Meli, M. Peruzzini, and F. Zanobini, J. Chem. Soc., Chem. Commun. 1987, 971.

HIGHLY CATALYTIC C-H ACTIVATION IN THE PRESENCE OF  $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ 

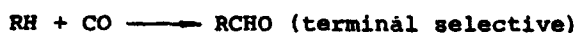
Masato TANAKA and Toshiyasu SAKAKURA, National Chemical Laboratory for Industry, Higashi, Tsukuba, Ibaraki 305, Japan

Direct functionalization of arenes and alkanes has been realized via C-H bond activation in the presence of transition metal complexes under irradiation. Rhodium complexes, in particular,  $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ , are powerful catalysts for the following reactions

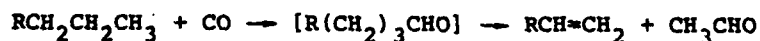
## (1) Carbonylation of arenes



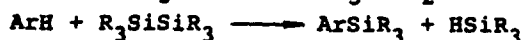
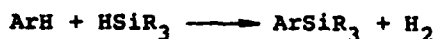
## (2) Carbonylation of alkanes



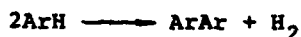
Depending on the wavelength, the reaction gives terminal alkenes and acetaldehyde:



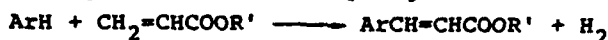
## (3) Silylation of arenes



## (4) Dehydrogenative homo-coupling of arenes



## (5) Dehydrogenative cross-coupling of arenes and alkenes



## (6) Dehydrogenation of alkanes giving alkenes



## (7) Schiff base synthesis



Some of these reactions are highly catalytic (turnover frequencies more than  $200\text{h}^{-1}$ ). Some aspects of the reaction mechanism including the effects of ligands and the role of irradiation will be discussed.

## References

- M. Tanaka et al., Chem. Lett., 1987, 249, 859, 1113, 2211, 2373, 2375; 1988, 155, 263. J.C.S. Chem. Commun., 1987, 758.

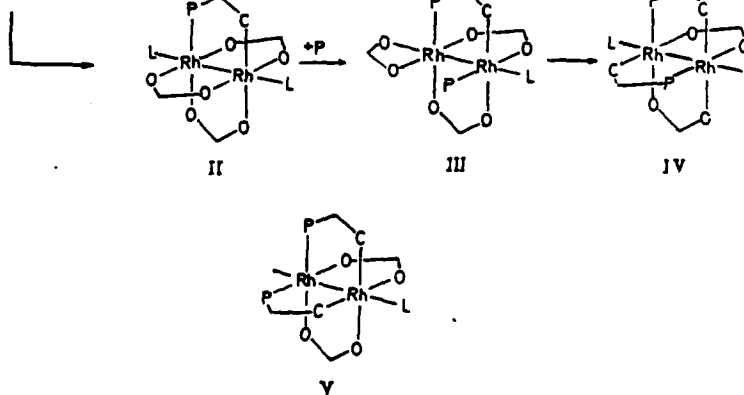
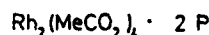
## NEW ORTHOMETALATION REACTIONS IN DIRHODIUM (III) COMPOUNDS

PASCUAL LAHUERTA, JORGE PAYA, M. ANGELES UBEDA

Depto. Química Inorgánica, Universidad de Valencia, Dr. Moliner, 50, 46100 BURJASSOT-VALENCIA.

Orthometalated arylphosphines have been shown to be good bridging ligands in dinuclear  $Rh_2^{4+}$  (1). Following our studies of orthometalation reactions in binuclear rhodium compounds (2), we report here the chemical behaviour of dirhodium tetraacetate adducts,  $Rh_2(O_2CCH_3)_4 \cdot 2P(I)$ ,  $P=PMe_2Ph(Ia)$ ,  $PMePh_2(Ib)$  and  $P(p-XC_6H_4)_3$  [ $X=H(Ic)$ ,  $CH_3(Id)$ ,  $Cl(Ie)$ ]. All these adducts generate doubly metalated compounds  $Rh_2(O_2CCH_3)_2(P-C)_2$  of type IV. By careful modification of the reaction conditions, intermediates of type II and III have been isolated in variable yields. The intermediate III, that contains a phosphine occupying an equatorial coordination site, is stabilized for less bulky P-donor ligands.

The reactivity of these intermediate compounds has been studied. In the presence of 2:1 molar excess of the corresponding phosphine, compound of type II ( $PPh_3$ ,  $PMePh_2$ ) readily reacts at room temperature yielding the corresponding doubly metalated IV. Similar reactivity is found for compound III ( $PPh_3$ ,  $PMe_2Ph$ ). Doubly metalated compounds with head to head configuration, structure V, have also been prepared. Additional aspects related to these particular reactions will be discussed.



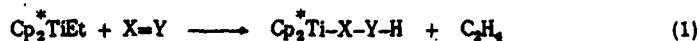
## REFERENCES.

- 1-Chakravarty, A.R.; Cotton, F.A.; Tocher J.M., *Organometallics* 1985, 4, 8.
- 2-Barceló, F.A.; Cotton, F.A.; Lahuerta, P.; Senáu, M.; Schwotzer, W.; Ubeda, M.A., *Organometallics*, 1987, 6, 1105 and references therein.

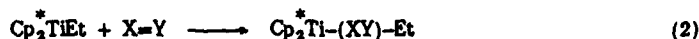
ACTIVE  $\beta$ -HYDROGEN IN  $\text{Cp}_2^*\text{TiR}$  COMPOUNDS

G.A. Luinstra and J.H. Teuben, Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands.

Thermally labile  $\text{Cp}_2^*\text{TiEt}$  1 ( $\text{Cp}^* : \eta^5\text{-C}_5\text{Me}_5$ ) reacts with unsaturated substrate molecules under the liberation of ethene (1).



Heteronuclear unsaturated molecules ( $t\text{-BuCN}$ ,  $\text{CO}_2$ ) and 2-butyne follow reaction 1 with formation of imide, formate and alkenyl  $\text{Cp}_2^*\text{Ti(III)}$  derivatives. Only in a few cases insertion into the metal-carbon bond is observed. In reaction with  $\text{CO}$ ,  $t\text{-BuNC}$  and paraformaldehyde 1 was transformed into acyl, iminoacyl and alkoxide derivatives (2).



Reaction 1 is also observed for interaction of  $\alpha$ -olefines with 1 (3).



For propene the equilibrium constant (278 K) was determined ( $K = 0.033$ ,  $\Delta G = 1.9$  Kcal/mol). As a consequence these  $\text{Ti(III)}$  compounds are not active in the polymerization of  $\alpha$ -olefines. A similar reaction was observed with other  $\alpha$ -olefines, but internal olefines (2-hexene) sterically demanding olefines (cyclohexene, styrene) and acetylenes (diphenylacetylene) do not react, probably for steric reasons.

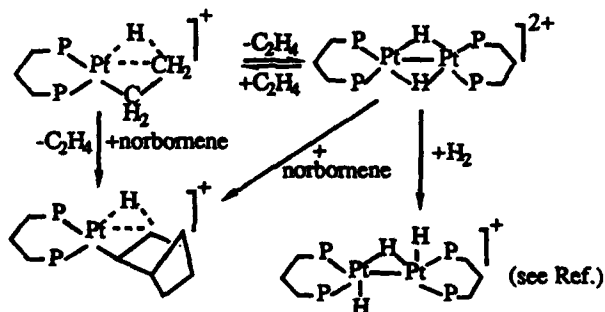
The mechanism of reaction 1 (and 3) is likely to involve a six-membered transition state in which a hydrogen atom is directly transferred from an ethyl-ligand to the substrate molecule.

## TWO-ELECTRON, THREE-CENTRE BONDING IN PLATINUM ETHYL DIPHOSPHINE COMPLEXES

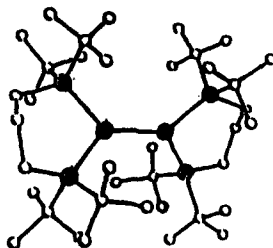
Nicholas Carr,<sup>a,b</sup> Laura Mole,<sup>a</sup> A Guy Orpen,<sup>b</sup> Alan D Redhouse,<sup>a</sup> and John L Spencer<sup>a</sup><sup>a</sup> Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT, UK<sup>b</sup> Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, UK

Protonation of  $[\text{Pt}(\text{C}_2\text{H}_5)_2(\text{Bu}^t_2\text{P}(\text{CH}_2)_3\text{PBu}^t_2)]$  affords the off-white crystalline complex  $[\text{Pt}(\text{C}_2\text{H}_5)(\text{Bu}^t_2\text{P}(\text{CH}_2)_3\text{PBu}^t_2)]^+ \text{X}^-$  where  $\text{X}^- = \text{BF}_4, \text{CF}_3\text{SO}_3, (\text{CF}_3\text{SO}_2)_2\text{CPh}$ . This formally 14-electron complex has been shown by  $^{13}\text{C}$ ,  $^1\text{H}$  and  $^{31}\text{P}$  nmr to be stabilised by a two-electron, three-centre agostic  $\text{Pt}-\text{H}-\text{C}$  bond. Remarkably the system is extremely fluxional even at low temperatures resulting in equivalence not only of all five ethyl protons but also of the  $\text{C}_\alpha$  and  $\text{C}_\beta$  via  $\beta$ -elimination and alkene rotation.

Scheme 1



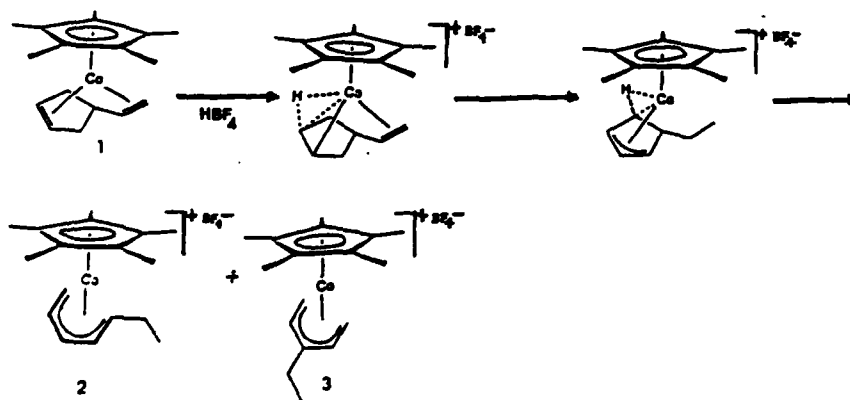
$\beta$ -agostic complexes can be viewed as models for the intermediate stage of  $\beta$ -elimination and alkene insertion; most importantly, the complex  $[\text{Pt}(\text{C}_2\text{H}_5)(\text{Bu}^t_2\text{P}(\text{CH}_2)_3\text{PBu}^t_2)]^+$  has been shown to undergo alkene exchange (see Scheme 1) and dimerisation with loss of ethylene to form a hydride bridged platinum dinuclear complex  $[\text{Pt}_2(\mu\text{-H})_2(\text{Bu}^t_2\text{P}(\text{CH}_2)_3\text{PBu}^t_2)_2][\text{BF}_4]_2$  (Scheme 1 and Figure 1).



## CARBON-CARBON BOND CLEAVAGE IN AGOSTIC COBALT COMPLEXES

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Carbon-carbon bond activation by soluble transition metal complexes remains one of the most prominent challenges in organometallic chemistry (Ref.). We have observed examples of facile carbon-carbon cleavage by the protonation of  $[\text{Co}(\eta\text{-C}_5\text{R}_5)(\text{diene})]$  complexes. For example protonation of  $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\eta^4\text{-bicyclo[2.2.2]octa-2,5-diene})]$  with  $\text{HBF}_4$  leads to  $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(1\text{-}3,7,8\text{-}\eta\text{-}5\text{-vinylcyclohexenyl})]\text{BF}_4$  via an agostic intermediate, and  $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\eta^4\text{-}4\text{-vinylcyclopentene})]$  (1) affords *syn*- $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\eta^5\text{-}1\text{-Et-C}_5\text{H}_6)]\text{BF}_4$  (2) and  $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\eta^5\text{-}3\text{-EtC}_5\text{H}_6)]\text{BF}_4$  (3) on protonation (Scheme). The structure of (2) was confirmed by a single crystal X-ray diffraction study.



Scheme

Reference: John E Bercaw, et al., *J Am Chem Soc*, 1988, 110, 976-987.



EVIDENCE FOR METAL-PHOSPHORUS  $\sigma$ - $\pi$  BACKBONDING IN

## THE BRIDGE-CLEAVAGE PRODUCTS OF CYCLOMETALLATED TRIMESITYLPHOSPHINE COMPLEXES

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The very bulky trimesitylphosphine ligand ( $P(mes)_3$ ) promotes formation of the cyclometallated dimeric complexes,  $[M(P^*C)X]_2$  ( $M=Pd, Pt$ ;  $P^*C=Pmes_2C_6H_2(CH_3)_2CH_2$ ;  $X=Cl, Br, I$ ), which undergo facile bridge-cleavage reactions with smaller tertiary phosphine ligands to give trans- $[M(P^*C)(PR_3)X]$ . Trends observed for the  $^1H$  and  $^{31}P$  NMR of these monomers strongly suggest a  $\pi$ -backbonding component in the  $M-PR_3$  bond whereas there is no evidence for a similar effect in the  $M-P$  bond of the parent dimers. Discussion is also extended to the related apparent order of trans-effect for the series of  $PR_3$  ligands studied.

SYNTHESIS AND REACTIVITY OF MESITYLENE-OSMIUM(0)  
AND MESITYLENE-HYDRIDO-OSMIUM(II) COMPLEXES:  
POTENTIAL PRECURSORS FOR C-H-BOND ACTIVATION ?

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Würzburg, Am Hubland, D-8700 Würzburg

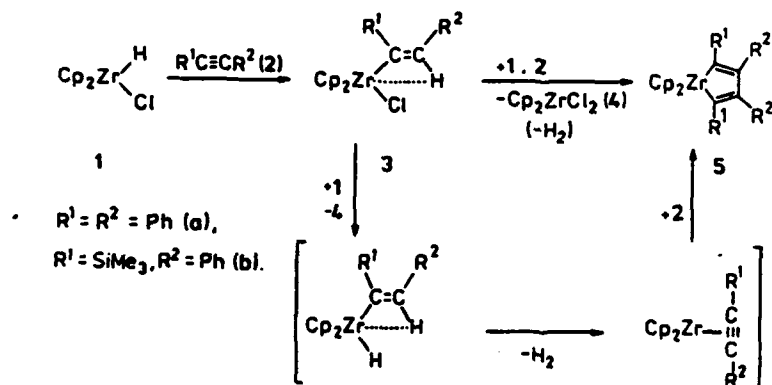
Starting with the easily accessible polymeric compound  $[(\text{mes})\text{OsCl}_2]_n$  a series of half-sandwich type mesitylene-osmium complexes have been synthesized. The first examples of mesitylene-osmium(0) derivatives  $(\text{mes})\text{OsLL}'$ , which contain two monodentate  $\pi$ -acceptor ligands, are prepared by several independent routes.

Reaction of  $(\text{mes})\text{OsCl}_2(\text{L})$  with suitable reducing agents gives the dihydrido complexes  $(\text{mes})\text{OsH}_2(\text{L})$ . The new compounds are considered to be potential precursors for generating a 16-electron intermediate  $[(\text{mes})\text{Os}(\text{L})]$ , able to activate C-H-bonds of aromatic or aliphatic hydrocarbons.

**Formation of a  $\beta$ -CH-Agostic Alkenylzirconocene Complex  
and Metallacyclopentadienes by Hydrozirconation of  
Alkynes**

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The reaction of  $\text{PhC}\equiv\text{CPh}$  (2a) with  $\text{Cp}_2\text{ZrHCl}$  (1) does not afford the anticipated alkenylzirconocene complex (3a), but a 1:1 mixture of metallacycle (5a) and  $\text{Cp}_2\text{ZrCl}_2$  (4). The formation of the "agostic" complex (3b) as well as the metallacycle (5b) and (4) from the reaction of  $\text{PhC}\equiv\text{CSiMe}_3$  (2b) with (1) leads us to propose that "agostic" alkenylzirconocene complexes may be important intermediates in this unexpected hydrozirconation.



With less sterically demanding alkynes, e.g.  $\text{HC}\equiv\text{CH}$ ,  $\text{PhC}\equiv\text{CH}$ ,  $\text{MeC}\equiv\text{CMe}$ , and  $\text{HC}\equiv\text{CSiMe}_3$ , (1) reacts to afford the normal alkenylzirconocenes.

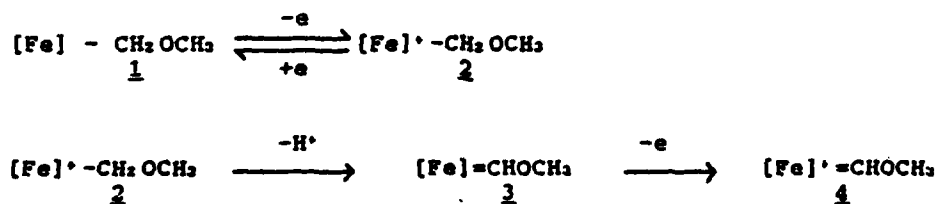
THREE STEPS PATHWAY FOR AN  $\alpha$ -HYDRIDE ABSTRACTION FROM IRON ALKYL.

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Loïc Toupet, Laboratoire de Physique Cristalline, UA CNRS 804, Université de Rennes I, 35042 Rennes Cedex, France.

Electron transfer pathway are of general interest in C-H bond activation of metal alkyl intermediates in a variety of catalytic reactions. It has been scarcely shown that C-H bond activation from transition metal alkyl gives rise to hydride transfer to the trityl cation as hydride acceptor by a two-step, electron transfer, hydrogen atom transfer, mechanism.

The first example of hydride abstraction from the iron methoxymethyl compound 1 through a three step pathway : electron transfer, proton abstraction, electron transfer (Scheme I) will be presented. The X-ray structure of the paramagnetic complex 2 will be also reported.



Scheme I

These reactions provide a new synthetic way to secondary heterocarbene compounds.

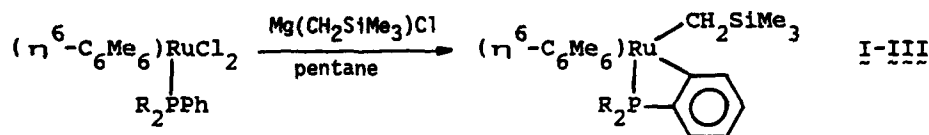
# TRIMETHYLSILYLMETHYL DERIVATIVES OF RUTHENIUM(II) WITH ORTHO-METALLATED PHOSPHINES

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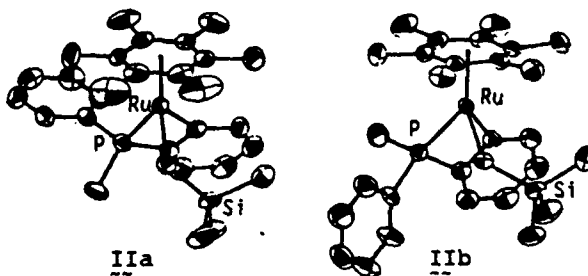
Cyclometallation reactions have attracted renewed interest since the discovery that some transition metal centers can insert into C-H bonds of hydrocarbons [1].

We have recently observed a new cyclometallation reaction in some ruthenium(II) systems leading to neopentyl derivatives containing *ortho*-metallated phosphines. With the aim to verify the generality of these reactions, we shifted to the trimethylsilylmethyl systems. In spite of the reduced steric hindrance of the alkyl group, the complexes  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)(\text{PPhR}_2)]$  do react with an excess of trimethylsilylmethyl Grignard reagent to give the *ortho*-metallated complexes I ( $\text{R} = \text{Ph}$ , 25% yield), II ( $\text{R}_2 = \text{MePh}$ , 28% yield), and III ( $\text{R} = \text{Me}$ , 5% yield):



II has been separated by column chromatography into the two diastereomers IIa (24% yield) and IIb (4% yield).

The structures of I-III have been unambiguously determined by X-ray crystal structure analysis. All complexes have a "three-legged piano stool" structure, with the *ortho*-metallated ring planar and practically co-planar with the benzene ring. In the Figure the Ortep projections of the diastereomers IIa and IIb are reported.



[1] G.W. Parshall, *Chem. Tech.*, **14**, 628 (1984).

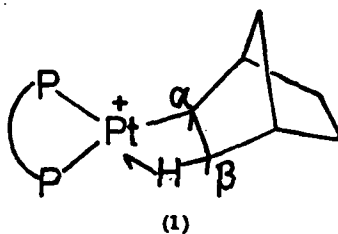
**Models for the  $\beta$ -elimination Reaction: Cationic Norbornyl Diphosphine  
Platinum and Palladium Complexes.**

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<sup>b</sup> Department of Chemistry and Applied Chemistry, University of Salford, Salford  
M5 4WT, UK

We have prepared a series of cations (1) in compounds of general formula  $[M(\text{norbornyl})(\text{diphosphine})]Y$ , where M is Pt or Pd, Y is  $\text{BF}_4$ ,  $\text{BPh}_4$  and the diphosphine is  $\{\text{Bu}_2\text{P}(\text{CH}_2)_n\text{P}^t\text{Bu}_2\}$ ,  $\{\text{cyh}_2\text{P}(\text{CH}_2)_n\text{P}^t\text{cyh}_2\}$  ( $n = 2$  or  $3$ ; cyh = *cyclo*- $\text{C}_6\text{H}_{11}$ ) or  $\{o\text{-(}^t\text{Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_4\}$ . In these species the norbornyl ligand is bound to the metal by both 2c-2e  $\sigma$ -alkyl and 3c-2e  $\beta$ -C-H (agostic) interactions.



We have studied the geometry and solution dynamics of cations (1) by multinuclear n.m.r. spectroscopy and X-ray diffraction. The extent of the  $\beta$ -agostic interaction may be monitored by examination of the P-H, Pt-H, Pt-P and C-H coupling constants. These show that the strength of the agostic (M-H-C) bond varies substantially as a function of both diphosphine chelate ring size and phosphorus substituent bulk. In addition, variable temperature n.m.r. spectra are consistent with an intramolecular rearrangement process, involving  $\beta$ -hydrogen elimination and olefin rotation, which is rapid at room temperature. X-ray crystal structure analyses of these compounds provide a second means of assessing the degree of  $\beta$ -C-H interaction, and complement the n.m.r. studies.

We view the agostic alkyls in cations (1) as models for the intermediate stages of the  $\beta$ -elimination/olefin-insertion reactions, an analogy which is strengthened by the observation of these reactions in the chemistry of these species. The studies we report allow detailed inspection of the course of these reactions.

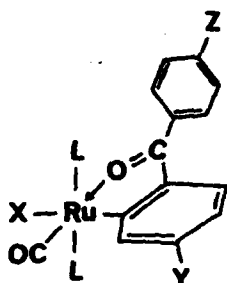
## Unusual C-H Activation Reactions of Ruthenium(0)

Michelle Stell, Madeleine Helliwell and Roger Mawby

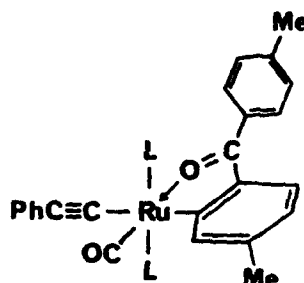
Department of Chemistry, University of York, York YO1 5DD, England

Complexes  $[\text{Ru}(\text{CO})_2\text{RP}'\text{L}_2]$  ( $\text{L} = \text{PMe}_2\text{Ph}$ ;  $\text{R}, \text{R}' = \text{methyl or aryl}$ ) decompose intramolecularly in propanone or benzene to give ketones  $\text{RCOR}'$  in good yield. Kinetic and mechanistic studies indicate a mechanism involving reductive elimination from intermediates  $[\text{Ru}(\text{CO})(\text{COR})\text{R}'\text{L}_2]$ . In the presence of halogen-containing compounds ( $\text{CHCl}_3$ ,  $\text{EtBr}$ ,  $\text{EtI}$ ), however, the diaryl complexes  $[\text{Ru}(\text{CO})_2(\text{C}_6\text{H}_4\text{Y}-4)(\text{C}_6\text{H}_4\text{Z}-4)\text{L}_2]$  ( $\text{Y} = \text{Z} = \text{H, Me or Cl}$ ;  $\text{Y} = \text{Cl}$ ,  $\text{Z} = \text{H or Me}$ ) yield the ortho-metallated complexes (1), where  $\text{X} = \text{halogen}$ . We believe that these are formed by reversible activation of a C-H bond in intermediate ruthenium(0) ketone complexes  $[\text{Ru}(\text{CO})\{\text{OC}(\text{C}_6\text{H}_4\text{Y}-4)(\text{C}_6\text{H}_4\text{Z}-4)\}\text{L}_2]$  followed by reaction of the resulting hydride complexes  $[\text{Ru}(\text{CO})\{\text{OC}(\text{C}_6\text{H}_3\text{Y}-4)(\text{C}_6\text{H}_4\text{Z}-4)\}\text{HL}_2]$  with the halogen-containing compounds.

Decomposition of  $[\text{Ru}(\text{CO})_2(\text{C}_6\text{H}_4\text{Me}-4)_2\text{L}_2]$  in the presence of  $\text{PhC}\equiv\text{CH}$  results in the formation of complex (2). Here both the ketone and the alkyne have undergone activation of a C-H bond.



(1)

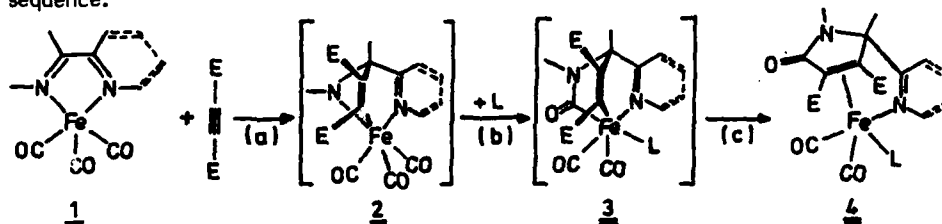


(2)

PREPARATION AND PROPERTIES OF (1,4-DIAZA-1,3-DIENE)  $\text{Fe}(\text{CO})_2(\text{CNR})$  AS CANDIDATES TO PROBE THE COMPETITIVENESS OF CO vs. CNR INSERTION.

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The reaction of  $(\text{DAD})\text{Fe}(\text{CO})_3$ , 1 (DAD=1,4-diaza-1,3-diene), with dipolarophiles has been shown to give 1,5-dihydropyrrrol-2-one complexes 4 [1] via the indicated reaction sequence.



(a) oxidative 1,3-dipolar cycloaddition of alkyne to the  $\text{C}=\text{N}-\text{Fe}$  unit. (b) CO-insertion.  
(c) reductive elimination (1,2 shift) and recoordination.

Structural types 2 [2] and 3 [3] could be stabilized in particular cases and have been identified by single crystal X-ray analysis. In order to probe the competitiveness of CO and CNR in the migration-insertion step (b) we have prepared some mono-isocyanide derivatives of 1 through Pd-catalyzed CO-substitution. The preparation of  $(\text{DAD})\text{Fe}(\text{CO})_2(\text{CN}-t\text{Bu})$ , 5, will be reported and their spectroscopic properties (IR,  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR) discussed. Contrasting 1, where CO scrambling is fast on the NMR time scale down to the lowest temperatures, intramolecular ligand exchange in 5a (DAB:  $i\text{Pr}-\text{N}=\text{CH}-\text{CH}=\text{N}-i\text{Pr}$ ) is slow at or below room temperature. Two different isomers in unequal amounts can be distinguished in the  $^{13}\text{C}$ -NMR spectra. This has to be taken into account when looking at CO vs. CNR insertion since only ligands in cis position to the migrating group can be inserted. Investigations on the reactivity of 5 in the above reaction sequence are now underway, and the latest results will also be presented.

- 1 H.-W. Fröhuf, F. Seils, M.J. Romão, R.J. Goddard; *Angew. Chem. Int. Ed. Engl.* **22** (1983) 992.
- 2 H.-W. Fröhuf, F. Seils, C.H. Stam; to be published.
- 3 H.-W. Fröhuf, F. Seils, R.J. Goddard, H.J. Romão; *Organometallics* **4** (1985) 948.



THE REACTIVITY OF THE TERTIARY PHOSPHINE COMPLEXES  
OF NICKEL(II) TOWARDS ALKOXIDES AND CARBON  
MONOXIDE.

by

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The reactions between tertiary phosphine complexes of formula  $\text{Ni}(\text{PEt}_n\text{Ph}_{3-n})_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and the alkoxides  $\text{RO}^-$  ( $\text{R} = \text{Me}, \text{Et}, \text{Ph}, \text{n-But}$ ) under a carbon monoxide atmosphere at room temperature and atmospheric pressure have been investigated. The products of the reaction depend from the nature of both the tertiary phosphine and the alkoxide. Carbonyl-alkoxo complexes of formula  $\text{NiL}_2\text{X}(\text{COOMe})$  ( $\text{L} =$  tertiary phosphine) have been obtained with methoxide ( $\text{MeO}^-/\text{Ni} = 1$ ), in yields strongly increasing with the basicity of the phosphine. These complexes react further with nucleophiles such as methoxide or aliphatic primary amines yielding phosphine-substituted nickel(0) carbonyl complexes and dimethyl oxalate and dimethylcarbonate or carbamates. Several organic compounds, including aldehydes and hydrocarbons, besides carbon dioxide and  $\text{Ni(II)}$  and  $\text{Ni(0)}$  derivatives, have been obtained with other alkoxides. The mechanism of the reactions investigated will be discussed.

This work was supported by C.N.R. Rome.

STEREOCHEMISTRY OF CARBON MONOXIDE INSERTION IN ALKYL COMPLEXES  
OF IRON (II) AND RUTHENIUM (II).

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Canada K7L 3N6

The stereochemistry of the insertion of carbon monoxide in the complexes  $M(CO)_2L_2RX$  ( $M=Fe,Ru$ ;  $X=I,CN,NCS$ ) was studied by  $^{13}C$  NMR spectra of variously labeled complexes. The effect of the trans substituent on the chemical shifts and the values of the trans C-C coupling constants with respect to the cis ones are important for structural assignment.

For the iron complexes we observed a strong trans effect on the chemical shifts of the carbonyl groups and a moderate effect on the coupling constants ( $J_{C-C}(cis)=4-8$  Hz,  $J_{C-C}(trans)=12-16$  Hz). On the contrary, for the ruthenium complexes, we observed a weak effect on the chemical shifts and a strong effect on the coupling constants ( $J_{C-C}(cis) \leq 1$  Hz;  $J_{C-C}(trans)=22-26$  Hz). These results allow us to assign the  $^{13}C$  NMR bands to the various carbonyl substituents and so to study the stereochemistry of the carbonylation reaction. The carbonylation of  $Fe(CO)_2(PMe_3)_2MeX$  ( $X=I,CN,NCS$ ) with  $^{13}CO$  gives both the isotopomers with the labeled CO in trans or in cis with respect to the acetyl group. The carbonylation of  $Ru(CO)_2(PMe_3)_2MeX$  ( $X=I,CN$ ) with  $^{13}CO$  is more stereospecific and gives only the isotopomer with the labeled CO trans to the acetyl group. These results are interpreted, contrary to the conclusions of the literature,<sup>2</sup> on the basis of methyl group migration with probable formation of square pyramidal intermediates. The relative thermodynamic stability of the intermediates is responsible of the distribution of the isotopomers. Although both ruthenium<sup>3</sup> and iron<sup>4</sup> dihaptoacyl structures were characterized being more stable than the unsaturated intermediates, they are not important to explain the stereochemistry of the carbonylation.

Work Supported by MPI, Rome, Italy

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- 2) M. Pankowski, M. Bigorgne, *J. Organometal. Chem.*, **251**, 333 (1983).
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- 4) G. Cardaci, G. Bellachioma, P. Z. Zanazzi, *Organometallics*, **7**, 172 (1988).

## INDEX OF AUTHORS

PAPER NUMBER BOLD FACED: Presenter  
PAPER NUMBER NORMAL FACED: Coauthor

ABAD J.-A. 236	ARCE A.J. 46 71 75
ADAMS C.M. 325	ARIF A.M. 313
ADOVASIO V. 442	ARIF M. <b>353</b>
AHLGREN M. 98	ASCENZI P. <b>28</b>
AIME S. 47 388 390	ASDAR A. 408
AIRINEI A. 228	ASHBY J.R. 92
AKKERMAN O.S. <b>32</b> 142	ASHMAWY F.M. 356
ALBANO V.G. 4 96	ASTLEY S.T. <b>72</b>
ALBÉNIZ A.C. 276	ASTRUC D. <b>123</b>
ALCOCK N.W. 281	ASUNTA T. <b>395</b>
ALIBRANDI G. 113	ATTANASIO D. 269
AL-JUAID S.S. 217	AUL R. <b>305</b>
ALPER H. 368	
ALT H.G. <b>152</b>	
ALYEA E.C. 204 438	
AMANN S. 132 <b>245</b>	BACCANTI M. <b>312</b>
AMARASEKERA J. 3	BACHMANN B. 421
AMATORE C. 170	BAEV A. <b>352</b>
AMMANN C. 76	BAIRD M.C. 447
ANCIAUX A.J. 370	BAJAJ P. 252
ANDERSON T.J. 165	BALCH A.L. <b>31</b>
ANDREEVA N.I. 226	BALDENIUS K. 371
ANDRYUSHIN O. 107	BARTSCH R. 125
ANEMA S. 160	BASALGINA T.A. 140
ANKLIN C. 76	BASHILOV V.V. 220
ANTIÑOLO A. 188	BASOLO F. 117
ANTONOVICH V.A. 229	BASSET J.M. 199
ANTONSSON T. 104 374	BATES R.S. <b>333</b>
ANTSYSHKINA A.S. 366	BATTAGLIA L.P. 300
ARA I. 283	BAUM G. 133
ARCADI A. 308	BAXTER J.C. 278
ARCAS A. 292	BAYÓN J.C. 197

BECKER B. 87  
 BELETSKAYA I. 212  
 BELFORTE A. 426  
 BELLACHIOMA G. 447  
 BELSKY V.K. 49  
 BELT S.T. 120  
 BELY A. 107  
 BENDER B.R. 346  
 BENNETT M.A. 151 282  
 BENTLEY G.W. 102  
 BENYUNES S.A. 319  
 BERGAMINI P. 281  
 BERGDAHL M. 5  
 BERINGHELLI T. 382  
 BERLITZ TH.F. 253  
 BERMEJO M.-J. 273  
 BERMUDEZ M.-D. 293  
 BERNOCCHI E. 308  
 BERRY D.E. 282  
 BERTANI R. 9 277  
 BERTONCELLO R. 346  
 BERTOZZI S. 106  
 BESANÇON J. 419  
 BHARGAVA S.K. 282  
 BHATIA S. 219  
 BIAGINI P. 369  
 BIANCHINI C. 198 432  
 BICKELHAUPT F. 32 142  
 BITTERWOLF T.E. 148  
 BLANCHARD H. 191  
 BLISS T. 405  
 BLOM R. 91  
 BLÜMEL J. 126 213  
 BOAG N.M. 56  
 BOCHKAREV L.N. 295 412  
 BOCHKAREV M.N. 140  
 BOCHMANN M. 257 376  
 BODIGUEL J. 264  
 BOERSMA J. 275  
 BOESE R. 65

BOIS C. 53  
 BONATI F. 89 235  
 BONDAREVA V.L. 150  
 BOOIJ M. 139  
 BORDONI S. 167  
 BORGDORFF J. 100  
 BORRACHERO M.V. 292  
 BORTOLIN R. 178  
 BORZANI G. 345  
 BOSCHI T. 30  
 BOTT S. 191 401  
 BOTTA M. 47 385 388 390  
 BOVIO B. 89  
 BOYADJIEV B. 406  
 BRADFORD M.R. 44  
 BRAGA D. 16 73 96  
 BRAY J. 59  
 BREGADZE V.I. 229  
 BRÉGAINT P. 326  
 BREKAU U. 336  
 BRESSAN M. 86  
 BRIANESE N. 413  
 BRODT G. 124  
 BROOKHART M. 39  
 BROWN M.P. 400  
 BROWN S.S.D. 178  
 BRUNEAU C. 427  
 BRUNO G. 97  
 BRUNORI M. 28  
 BUCHLER J.W. 27  
 BÜCHNER K. 159  
 BUKALOV S.S. 424  
 BUMAGIN N. 212  
 BURINI A. 89 308  
 BURKE M.R. 346  
 BURLAKOV V. 147  
 BURNS D. 400  
 BURROWS A. 401  
 BUSATO S. 377  
 BUSETTO L. 167

BUSYGINA I.N. 366

CACCHI S. 308  
CALDERAZZO F. 263 426  
CANO F.H. 276  
CARDACI G. 447  
CARLIER E. 355  
CARMONA E. 144  
CARR N. 172 436 443  
CARR S. 382-1  
CARTY A.J. 70 156  
CASARIN M. 346  
CASTIGLIONI M. 414  
CATALANO V. 31  
CATELLANI M. 209  
CAULTON K.G. 114 146 354  
CECCON A. 122 271 342  
CERIOTTI A. 42  
CESAROTTI E. 108  
CETINI G. 414  
CHANDLER V.L. 174  
CHEN H. 386  
CHEONG M. 117  
CHIANG M.Y. 189 265  
CHICOTE M.-T. 236 290 293  
CHIMICHI S. 325  
CHISHOLM M.H. 103  
CHIOUSOLI G.P. 209 300  
CHIZHOV Y.V. 248  
CHMIELECKA J. 36  
CHOJNOWSKI J. 34 36  
CHORIANOPOULOU M. 164  
CHOW P. 157  
CHRISTENSON B. 287  
CHVALOVSKÝ V. 110  
CIANI G. 382 399  
CINGOLANI A. 235  
CISERO M. 390

CLARK G.R. 78  
CLARK S. 92  
CLAVER C. 197  
CLODE K.E. 425  
COCKROFT J. 90  
COHEN H. 339  
COLLIGIANI A. 106  
COLOMBO B. 312  
CONAN F. 428  
CONOLE G. 311  
CONSIGLIO G. 196  
COOK G.K. 105  
CORRIU R. 87  
COSTA G. 418  
COSTA J.-L. 77  
COSTA M. 300  
COURET C. 135  
COWIE M. 367  
COWLEY A.H. 320  
COX D.N. 423  
CRAIG P.J. 92  
CRAVARITOU M. 164  
CROOK J. 59  
CRUZ-GARRITZ D. 337  
CSONKA G. 88  
CSÓREGH I. 173  
CUCCIOLITO M.E. 4  
CULLEN W.R. 291  
CUSUMANO M. 113  
CUTILLAS N. 57  
CYPRYK M. 34

DAKTERNIEKS D. 256  
D'ALFONSO G. 382  
DAMOUR D. 299  
DANY F. 199  
DARENSBOURG M.Y. 344  
DAVIDSON G. 50

DAVIES C. 50	DOSSI C. 35
DAVIES S.J. 383	DOZOROV A.V. 351
DAWSON R.H. 334	DRÄGER M. 135 240
DAY M. 46 71 385	DRÄGUTAN I. 239 365
DEACON G.B. 141	DRÄGUTAN V. 239 365
DE BOER H.J.R. 142	DRELA I. 338
DEEMING A.J. 71 75	DRUMZEE Y. 185
DE FELICE V. 4 309	DUCHATEAU R. 139
DE GRAAF W. 275	DUCKETT S.B. 62
DE HARO C. 57	DUFAUD V. 199
DE LANGE W. 445	DU MONT W.-W. 136
DELLA PERGOLA R. 14	DUNNE B.J. 21 172
DELLEDONNE D. 300	DU PLESSIS J.A.K. 363
DEL PINO C. 409	DU TOIT C.J. 363
DEL ZOTTO A. 84	DZHEMILEV U.M. 303
DEMARTIN F. 14 42	
DE MEL S. 129	
DEMONCEAU A. 77 355 370 429 430	
DE PAOLI G. 143 296	EABORN C. 217
DE RENZI A. 309	EDWIN J. 128
DES ABBAYES H. 200 357	EFFINGER G. 255
DE SANCTIS Y. 71 75	EGUREN L. 322
DEUBELLY B. 243 262	EHLERS J. 371
DEVENISH R. 40	EICHENBERGER E. 375 376
DEVORE D.D. 222	EISCH J.J. 93
DIAS A.R. 38 51 315	EISENSTEIN O. 18 354
DI BUGNO C. 80	EL-IDRISSI RACHIDI I. 18
DICKBREDER R. 85	ELSCHENBROICH C. 133
DI GIACOMO R. 256	ELSEVIER C.J. 69 270 389
DI GIORGIO P. 442	EL-SHEIKH M.Y. 356
DIJKHUIS D. 445	ENGEL D.W. 83
DITZEL E.J. 282	ENGELHARDT H.E. 152
DI VAIRA M. 175	ERCOLANI C. 28
DIVERSI P. 442	EREMENKO I.L. 49
DIXNEUF P.H. 193	ERKER G. 183 250 305 407 440
DOLBY P.A. 393	ERNST L. 171 171
DOLCETTI G. 362	ERNSTING J.M. 215
DOMRACHEV G.A. 261 379	ESCUPIE J. 135
DONG L. 174	ESPINET P. 37 276
DOSSETT S.J. 403	ETIENNE M. 43

EZOMO O. 401

FACCHIN G. 277  
FACHINETTI G. 369  
FAEGRI JR. K. 91  
FAJARDO M. 188  
FALORNI M. 182  
FANIZZI F.P. 7  
FARAONE F. 97  
FARNETTI E. 63  
FEDOROVA E.A. 140  
FEDYUSHKIN I.L. 295  
FEHLHAMMER W.P. 316 405 406  
FEHLNER T.P. 101  
FERNANDEZ-BAEZA J. 290  
FERRER M. 402  
FIELD J.S. 83 335  
FILIPPI F. 162  
FILIPPOU A.C. 153  
FISCHER E.O. 153  
FISH R.H. 6  
FLORENCIO F. 188  
FLORES J.C. 186  
FLORIS B. 344  
FLUCK E. 81  
FOCES-FOCES C. 276  
FOCHI G. 206  
FOLTING K. 354  
FONTAINE M. 111  
FONTAINE X. 382-1  
FORD P.C. 166  
FORNIÉS J. 283  
FORSYTH C.M. 141  
FOURNIER J. 427  
FOWLES E. 382-1  
FRAENKEL G. 180  
FRANCIS A.M.A. 83  
FREDIANI P. 198

FRENI M. 382  
FRÜHAUF H.-W. 445  
FUJII T. 23  
FUJIWARA Y. 301  
FUMAGALLI A. 96  
FUSI A. 35

GABLE R.W. 256  
GALLOP M.A. 392  
GAMASA M.P. 12  
GAMBARDELA M.T.P. 288  
GAMBARO A. 122 271 342  
GAMBAROTTA S. 189 265  
GAMBINO O. 397  
GARBUZOVA I.A. 424  
GARCÍA G. 57 274  
GARCÍA J. 274  
GARCIA M.H. 51 315  
GARCÍA ALEJANDRE J. 337  
GARCÍA ALONSO F.J. 380 381  
GARCÍA SANZ M. 380  
GARGANO M. 373  
GARLASCHELLI L. 14  
GASANOV R. 341  
GASDASKA J. 298  
GAUTHERON B. 264 419  
GAVRILOVA G.V. 304  
GEIGER W.E. 128  
GELLERT R.W. 385  
GEMEAY A.H. 356  
GEOFFROY G.L. 94  
GERVASIO G. 321 345 397  
GHEDINI M. 431  
GIACOMELLI G. 182  
GIANNOCARO P. 446  
GIELEN M. 86  
GIMENO J. 12  
GIOIA LOBBIA G. 235

GIURGIU D. 228  
GLASER E. 201  
GLUSHAKOVA V.N. 379  
GOBETTO R. 47 97 118 388 390  
GODOVIKOV N.N. 229  
GOGAN N.J. 168  
GOLUBINSKAYA L.M. 229  
GOMES P.C.B. 310  
GOROBETS E.V. 227  
GOTTARDI F. 122  
GOWDA N.M.N. 267  
GRAHAM W.A.G. 2  
GRANOZZI G. 346  
GRASSI M. 108  
GRAZIANI M. 63 362  
GREEN M. 118 311 319  
GREEN M.E. 56  
GREPIONI F. 73 96  
GRILLI E. 35  
GRIMSHIRE M.J. 319  
GROVE D.M. 364  
GUERCHAIS J.-E. 428  
GUERCHAIS V. 205 408  
GUÉRIN C. 87  
GUEUTIN C. 416  
GULDNER K. 391  
GULIŃSKI J. 64  
GUPTA B.D. 415  
GUPTA K.L. 241  
GUPTA V.D. 242  
GUTIERREZ-JUGO J.-F. 236

HAALAND A. 20  
HABIB A.M. 356  
HABUŠ I. 358  
HACKSELL U. 173  
HAFNER A. 325  
HAINES R.J. 83 335

HAJELA S. 118  
HÅKANSSON M. 286  
HAMON J.-R. 326  
HAMPEL B. 85  
HANIKA G. 131  
HARDCASTLE K.I. 46 71 385  
HARDING M.M. 393 400  
HARROD J. 185  
HART I.J. 221 410  
HÄRTER R. 376  
HAYMORE B.L. 298  
HE X.D. 95  
HEALY M.A. 340  
HEATON B.T. 13 40 42  
HECK J. 421  
HEEB U. 79  
HEIL B. 359  
HEINICKE J. 88  
HELLIWELL M. 444  
HELQUIST P. 211  
HENNER B. 87  
HERNÁNDEZ S. 320  
HERRMANN R. 134  
HERTKORN N. 126 213  
HESSEN B. 190  
HEUER L. 171 171  
HEUMANN A. 374  
HIETALA J. 327  
HILL A.F. 155 411  
HIRAMA K. 23  
HIRTH U. 132 251  
HITCHCOCK P.B. 61 125 217  
HOCK R. 250  
HODGSON D.J. 78  
HOFFMANN T. 321  
HOFFMEISTER H. 406  
HOGARTH G. 70 156  
HOLECEK J. 234  
HOLT E.M. 48  
HOLTMANN U. 85



HORSFIELD E.C. 83  
HORVÁTH I.T. 194  
HOSKINS B.F. 256  
HOSSAIN M.A. 191  
HOWARD J.A.K. 221 222 383 411  
HOWARD K.E. 3  
HOWDLE S.M. 340  
HRADIL J. 110  
HSY H.C. 11  
HUANG Y. 302  
HUBER B. 214  
HUBERT A.J. 77 111 355 370 429 430  
HUBERT-PFALZGRAF L.G. 184  
HUFFMAN J.C. 146 354  
HUGEL-LE GOFF C. 318  
HURLEY J. 133  
HURSTHOUSE M.B. 191  
HUTTNER G. 130

IBRAGIMOV A.G. 303  
IGGO J.A. 13  
IGLESIAS M. 409  
IMHOFF P. 270  
INGALLINA P. 42  
INGROSSO G. 442  
INOUE H. 81  
ISOBE K. 58

JAGGAR A.J. 257  
JAGNER S. 286  
JALÓN F. 188  
JANSEN R.-M. 331  
JAOUEN G. 232  
JAYASINGHE I.S. 168  
JEAN Y. 18  
JEANNIN Y. 53 185

JEFFERY J.C. 44 222 410  
JEFFREY J.G. 401  
JEGAT C. 145  
JENNY T.A. 121  
JHA N.K. 252  
JOBE I.R. 157  
JOHNSON B.F.G. 73 74 386 391 392  
JOHNSON T. 114  
JONES P.G. 236 290 292 293  
JONES W.D. 174  
JÖRG K. 246  
JOUSSEAUME B. 176  
JOVANOVIĆ-KOLAR J. 289  
JUSTINO J. 38  
JUTZI P. 85

KAGANOVICH V.S. 169  
KAIFER E. 249  
KALBARCZYK-BIDELSKA E. 215  
KALININA G.S. 140  
KANNE D. 85  
KARL U. 25  
KARSCH H.H. 131 214 243 262  
KASKA W.C. 207  
KAŠPAR J. 362  
KASTRUP R.V. 194  
KATSER S.B. 366  
KAUR G. 234  
KAUSHIK N.K. 219  
KAWASAKI Y. 10  
KEINAN E. 203  
KELLY K. 378  
KERNAGHAN S.A. 13  
KHATTAR R. 16 101 386  
KIM H.-S. 6  
KING R.B. 48 349  
KITAGAWA S. 284  
KIZAS O. 394

KLAPÖTKE T. 259 260  
KLÄUI W. 82  
KLEIN K.-D. 181  
KNORS C. 211  
KOELLE U. 65  
KOETZLE T. 114  
KÖHLER F.H. 126 213  
KONIS S. 164  
KOLLÁR L. 359  
KÖPF H. 258 259  
KÖPF-MAIER P. 259  
KOPRIVANAC N. 289  
KORIDZE A. 394  
KOSKIMIES S. 52  
KOSSAKOWSKI J. 65  
KOSTAS I.D. 216  
KRAAKMAN M.J.A. 384  
KRAMER A. 254  
KRAMER V. 289  
KRAVTSOV D.N. 268 422  
KREITER C.G. 79  
KRIVYKH V. 395  
KRÜGER C. 99  
KRUSIC P.J. 170  
KUBICKI J. 338  
KUBOTA M. 165  
KUDINOV A.R. 424  
KUDINOV R.R. 169  
KUROIWA T. 81  
KUROSAWA H. 10  
KUTCHIN A.V. 41 226 227  
KUTYRYOVA V.V. 261  
KUZNETZOV V. 107  
KWON H.B. 328

LACHMANN G. 363  
LAHUERTA P. 434  
LALAMA M. 129

LALINDE E. 37  
LAMBERTSEN T. 90  
LANFRANCHI M. 12 279  
LANGE L. 136  
LAPINTE C. 205 408 441  
LAPPERT M.F. 61  
LARDICCI L. 182  
LASCHI F. 47  
LASTRA E. 12  
LATRONICO M. 446  
LAURENT P. 200  
LAZRAQ M. 135  
LEE G.H. 54  
LEE S.K. 160  
LEFFERS W. 85  
LEHMKUHL H. 99  
LEISSNER J. 25  
LEONESI D. 235  
LEONI P. 80  
LEWIŃSKI J. 225  
LEWIS J. 73 74 386 391 392 396  
LEXA D. 29 416  
LI Y. 138  
LI Z.-H. 233  
LICOC CIA S. 30  
LIEBESKIND L. 298  
LIN C.-C. 329  
LIN I.J.B. 11  
LIN J.T. 54  
LINCOLN D. 39  
LINDNER E. 201 331  
LINDSTEDT E.-L. 5  
LIU L.-K. 329  
LOCKEMEYER J.R. 3  
LOKSHIN B.V. 424  
LONGATO B. 8  
LONGOBARDI M.G. 163  
LONGONI G. 42  
LÓPEZ G. 57 274  
LÓPEZ MARDOMINGO C. 188

LORÁND E. 248  
LORBERTH J. 253  
LORENZ I.-P. 26 254 255 272  
LORENZOTTI A. 235  
LO SCHIAVO S. 97  
LO STERZO C. 55  
LOWRY R.M. 410  
LU X. 302  
LUCAS C. 199  
LUCHERINI A. 442  
LUINSTRÁ G.A. 435  
LUMINI T. 423  
LUMME P.O. 169  
LUNDQUIST E.G. 146 354  
LUNNISS J. 73  
LUTSENKO Z.L. 268  
LYCKA A. 234

MAAH M.J. 125  
MACKAY K.M. 160  
MAERCKER A. 181  
MAISONNAT A. 95  
MAITLIS P.M. 58  
MAKAROV E.I. 351  
MAKSYMUK P. 127  
MALISCH W. 132 230 231 245 246 247  
249 251  
MALITO J. 204 438  
MANASSERO M. 14 42  
MANN B.E. 102  
MARCHETTI F. 442  
MARCHETTI M. 182  
MARCHIONNA M. 42  
MARCINIEC B. 64  
MARCOS M. 37  
MARDER T.B. 70 157  
MARESCA L. 280  
MAR'IN V.P. 420

MARINELLI F. 308  
MARINETTI-MIGNANI A. 317  
MARKIES P.R. 32 142  
MÁRKI M. 247  
MARKÓ L. 321  
MARKOVA S.A. 227  
MARKS T.J. 19 158  
MARQUEZ-SILVA R.-L. 355  
MARTINELLI M. 392  
MARTINENGO S. 14 96 399  
MARTINEZ J. 58  
MARTON D. 208  
MASARWA M. 339  
MASCETTI J. 145  
MASCIOCCHI N. 14 42  
MASKAEVA E.V. 220  
MASSA W. 133  
MASSEY A.D. 391  
MATARASSO-TCHIROUKHINE E. 232  
MÁTÉ M. 372  
MATHES M. 240  
MATHEY F. 192 317 318  
MATTSON M. 211  
MAURO A.E. 288  
MAWBY R. 59 332 444  
MAYER H.A. 207  
MAYR A. 404  
MAYS M.J. 387  
MAZANOVA L.M. 294  
MAZID M. 191  
MCCAMLEY A. 120  
MC CLURE D.S. 404  
MCDONALD III J.H. 105  
MCGEARY C.A. 217  
MCGRATH D. 298  
MCPARTLIN M. 311  
MCPHILLIPS T. 46 385  
MEANWELL N.J. 58  
MEETSMA A. 139 190  
MELI A. 198 432

MÉLOTTE M. 86  
 MENA M. 186  
 MERCIER F. 318  
 MERTIS C. 164 360  
 MESSELHÄUSER J. 282  
 MEUNIER P. 264 419  
 MEYER A. 246  
 MEYERSTEIN D. 116 339  
 MEZZETTI A. 84  
 MICHA-SCRETTAS M. 218  
 MICHELIN R.A. 9  
 MICHELIN LAUSAROT P. 414  
 MICHELS W. 79  
 MIDOLLINI S. 175  
 MIGINIAC L. 299  
 MIKHAILOV V. 352  
 MILLER J. 310  
 MILONE L. 388 390  
 MILOSZ M. 127  
 MINASSIAN H. 46  
 MINATO A. 301  
 MINGOS D.M.P. 401  
 MINNITI D. 113  
 MISHRA A.C. 252  
 MOBERG C. 104 374 417  
 MÖHRKE A. 85  
 MOISEEV I.I. 137 366  
 MOLE L. 172 436  
 MOMENTEAU M. 416  
 MONACELLI F. 28  
 MONSÚ SCOLARO L. 113  
 MORALES R.G.E. 404  
 MORAN P.J.S. 310  
 MORE P. 212  
 MORET M. 382 399  
 MORI N. 297  
 MORVILLO A. 66  
 MOULINES F. 123  
 MOZELESKI E.J. 194  
 MOZZON M. 9

MUL W.P. 69 389  
 MULLER F. 45 384  
 MÜLLER G. 126 131 179 214 243 262  
 MÜLLER U. 253  
 MULLEY S. 40  
 MUNAKATA M. 284  
 MUNZ C. 306  
 MURA P. 269  
 MURAI S. 10  
 MÜSSIG S. 25  
 MUTIN R. 199

NAGY Á. G. 330  
 NAGY-MAGOS Z. 321  
 NARDELLI M. 300 442  
 NATILE G. 7 280  
 NAWAR N. 323  
 NEGISHI E.-I. 187  
 NEHER A. 272  
 NELSON G.E. 223  
 NÉMETH L. 372  
 NEVE F. 431  
 NG M.M.P. 78  
 NICHOLLS J.C. 437  
 NICHOLSON B.K. 160  
 NICOLA G. 118  
 NIEF F. 192  
 NIKANOROV V.A. 304  
 NILSSON M. 5 286  
 NIXON J.F. 125  
 NOBILE C.F. 279 446  
 NODES E. 132  
 NOELS A.F. 77 111 355 370 429 430  
 NOHEDA P. 154  
 NOMOTO T. 32 142  
 NORTON J.R. 8 346  
 NOVIKOVA L.N. 422  
 NURUSHEV R.A. 41

NUTTON A. 58  
NYBURG S.C. 319  
NYULÁSZI L. 88

OHLSSON B. 119  
OJIMA I. 195 328  
OLIVEIRA J.A. 380  
OLIVER J.P. 129  
OLSSON T. 5 287  
OPERTI L. 414  
ORAMA O. 327  
ORLOV N.A. 412  
ORPEN A.G. 21 172 436 443  
ORTAGGI G. 163  
OSELLA D. 47 388 390  
OSKAM A. 161 324  
OSSOLA F. 413  
OSWALD A.A. 194  
OTERO A. 188  
OUATTARA I. 419  
OZASA S. 301

PAGLIARINI O. 184  
PAIARO G. 224  
PAKKANEN T.A. 98  
PALAZZI A. 167  
PALLAVICINI P. 263  
PÁLYI G. 398  
PAMPALONI G. 263  
PANDEY O.P. 266  
PANDOLFO L. 224  
PANUNZI A. 309  
PAOLESSE R. 30  
PAPIĆ S. 289  
PARBHOO B. 178  
PARKINS A.W. 319

PASINSZKY T. 88  
PASQUALI M. 80  
PASYNKIEWICZ S. 99 215 225  
PASYNSKII A.A. 350  
PASYNSKY A.A. 49  
PATRIKEEVA N.B. 261  
PAYA J. 434  
PAYNE G.F. 297- 1  
PEARSON R.G. 166  
PELIZZI C. 300  
PELIZZI G. 30 236  
PELLI B. 280  
PELLINGHELLI M.A. 186 279  
PENNESI G. 28  
PENYAGINA I.M. 140  
PEREGUDOV A.S. 268  
PEREYRE M. 307  
PÉREZ J. 37  
PERSSON M. 173  
PERUTZ R.N. 62 120  
PERUZZINI M. 175 198 432  
PETROVSKII P. 394  
PETZ W. 24  
PFEIFER S. 27  
PHILLIPS J.A. 70  
PIERGIOVANNI A. 279  
PIETRONI B.R. 89 308  
PIETRZYKOWSKI A. 127  
PILOTTI M.U. 221 222 383  
PIRODDI A. 182  
PLAIA U. 405  
POILBLANC R. 95  
POLIAKOFF M. 340  
POLO A. 197  
POMAZANOVA N.A. 422  
PONTI J.J. 274  
POPLAWSKA J. 99  
PORAJ-KOSHITS M.A. 366  
PORCHIA M. 413  
PORNET J. 299

PORTA C.C. 288  
POSTMA D. 139  
PRATI L. 108  
PREDIERI G. 68 300  
PREGOSIN P.S. 76  
PRI-BAR I. 368  
PRINGLE P.G. 281  
PRITZKOW H. 109 124 159  
PROKOPENKO YU.A. 41  
PSARO R. 35  
PSAROUDAKIS N 164 360  
PUNTAMBEKAR S. 149  
PURSIANEN J. 98

QIAN C. 138

RADKOV YU.F. 140  
RAITHBY P.R. 74 386  
RAMASWAMY Y.S. 267  
RAMIREZ J.A. 432  
RAMIREZ DE ARELLANO C. 236  
RAMLI E. 3  
RANGA T. 398  
RATH N.P. 101  
RAUCHFUSS T.B. 3  
RAUSCH M.D. 148  
RAVASIO N. 373  
RAZA Z. 358  
RAZUVAEV G.A. 140 379 420  
REAL J. 197  
REBER G. 214  
REDDY G.K.N. 267  
REDHOUSE A.D. 436 437  
REEDY JR. P.E. 31  
REEVE C. 311  
RÉFFY J. 88

REGER D.L. 278  
REICH W. 246  
REICHENBACH G. 447  
REIMER S. 31  
REINA R. 402  
REUTOV O.A. 304  
RHEINGOLD A.L. 128 322  
RICHESON D.S. 314  
RICHMOND T.G. 313  
RICHTERING V. 258  
RICKARD C.E.F. 78  
RIEDE J. 214  
RIERA V. 53 380 381  
RIGO P.L. 84  
RIX L.A. 335  
ROBALO M.P. 51 315  
ROBERT F. 185  
ROBERTSON G.B. 282  
ROBINSON B.H. 100 291  
ROGER C. 326 441  
ROHDE W. 115  
ROKHLINA E.M. 268  
ROMÁN E. 320  
ROMANOVA T.YU. 226  
ROMÃO C.C. 315  
ROMEO R. 113  
ROMERO A. 154  
ROPER W.R. 78  
ROS B. 37  
ROS R. 15  
ROSENBERG E. 118 385  
ROSSELL O. 402  
ROSSETTI R. 162 397  
ROSSETTO G. 413  
ROSSI M. 373  
ROTONDO E. 97  
ROULET R. 15 423  
ROVERI M.R. 288  
ROY M. 415  
ROY S. 415

ROYO P. 186  
ROZENBERG V.I. 304  
RUBEZHOV A.Z. 268  
RUBINSZTAJN S. 34  
RÜEGGER H. 76  
RUIZ A. 197  
RUIZ J. 274  
RUIZ M.A. 53 381  
RUPPLI U. 128  
RYBINSKAYA M.I. 169 395 424  
RYPDAL K. 20

SABAT M. 19  
SABO-ETIENNE S. 200  
SACCO A. 279 446  
SAEZ I.M. 58  
SAKAKURA T. 433  
SAKAMOTO K. 23  
SAKURAI H. 23  
SALA-PALA J. 428  
SALTERIS C.S. 216  
SALZER A. 128  
SAMAD S.A. 361  
SAMUEL E. 185  
SÁNCHEZ G. 274  
SANCHEZ L. 12  
SANCHEZ-DELGADO R.A. 355  
SANDERS N.H. 411  
SANDHU G.K. 234  
SANSONI M. 14 42  
SANTANA M.D. 57  
SANTI S. 271 342  
SANTOS A. 154  
SANTOS R.H.A. 288  
SANZ C. 188  
SANZ-APARICIO J. 188  
SAPPA E. 68 387  
SARJUDEEN N. 61

SATGÉ J. 135  
SAURA-LLAMAS I. 290  
SAVEANT J.-M. 29 416  
SAXENA G.C. 241  
SCHÄFER V. 124  
SCHÄUFELE H. 109  
SCHEFFOLD R. 375 376 377  
SCHENK W.A. 25  
SCHMEUSSER M. 132  
SCHMUTZLER R. 171 171  
SCHNEIDER A. 131  
SCHOBER U. 201  
SCHOMBURG D. 171  
SCHRÖDER A. 316  
SCHUBERT B. 90  
SCHUMANN H. 313 322  
SCHWAB R. 196  
SCIALIS R. 163  
SCRETTAS C.G. 216 218  
SECO M. 402  
SEELBACH W. 230  
SEGRE A. 269  
SEMCHIKOV YU.D. 294  
SERGEEV S.V. 304  
SERRANO J.L. 37  
SERRANO R. 186  
SERVICE M. 160  
SEUTET P. 211  
SEVERENGIZ T. 136  
SEWING D. 136  
SEYAM A. 19  
SHAFII B. 93  
SHAPOSHNIKOVA A.D. 49  
SHARMA U. 238  
SHAW B.L. 52 382-1  
SHIN S.H. 253  
SHIRAI T. 81  
SHIRIN Z. 361  
SHOCK L.E. 19  
SHUR V. 147

SHUSTOV S.B. 294	STRUCHKOV Y. 147
SICKINGER A. 201	STUFKENS D.J. 161 324
SIDDIQUI M.R.H. 361	STÜRMER R. 421
SIEBERT W. 124	SU H. 375 376
SIMPSON J. 100	SUARDI G. 15
SINGH N.K. 238	SUBRA R. 170
SINNING H. 253	SULLIVAN A.C. 191
SIRONI A. 382 399	SUNDERMEYER J. 83
SISAK A. 60 372	ŠUNJIĆ V. 358
SKORODUMOVA N.A. 379	SUVOROVA O.N. 261
SMITH A.K. 323 334 393 400	SUZUKAMO G. 210
SMITH J.D. 217	ŠVEC F. 110
SODHI G.S. 219	SYED-MUSTAFA S.N.A.B. 396
SOHÁR P. 330	SZEPES L. 248
SOKOLOV V.I. 150 220	SZYNKARCZUK J. 338
SOLANA I. 325	
SOLANS X. 402	
SOOS E. 321	
SOSNA F. 407	TAGLIATESTA P. 30
SOSTERO S. 281	TAGLIAVINI G. 208
SPENCER J.L. 172 436 437 443	TAIT P. 38
SPIESBERGER A. 255	TAKACS J. 321
SPILLETT C.T. 166	TAKAHASHI T. 187
SPINK W.C. 148	TAKATS J. 72 346
SPIRATOS M. 228	TAMURA M. 210
SQUIZANI LIVOTTO F. 343	TANAKA M. 433
SRIVASTAVA P. 241	TAPIA F. 320
STADNICHENKO R.A. 49	TAQUI KHAN M.M. 361
STAHL S. 439	TÁSCHLER C. 418
STANGHELLINI P.L. 162 397	TASI M. 398
STAŃCZYK W. 36	TAVAKKOLI K. 217
STEIN E. 343	TAVARÈS P. 264
STELL M. 444	TAYLOR N.J. 70 156 157
STILLE J.K. 55	TAYLOR O.J. 177
STONE F.G.A. 155 221 222 383 403 410 411	TERRILL N. 56
STOPPIONI P. 175	TEUBEN J.H. 139 190 435
STRAWCZYNSKI A. 15	THEOPOLD K.H. 314
STREIB W. 354	THÉPOT J.-Y. 205
STROMNOVA T.A. 366	THEWALT U. 260
	THIVOLLE-CAZAT J. 199



THOMAS B.J. 314	
THORNTON-PETT M. 382-1	
THUM G. 230	
TINEMBART O. 377	VAARTSTRA B.A. 367
TIRIPICCHIO A. 12 68 186 380 381 387	VACCA A. 432
431	VAGLIO G.A. 414
TIRIPICCHIO-CAMELLINI M. 380 381	VAHRENKAMP H. 67
387	VALENCICH T. 22
TIROUFLET J. 419	VALLE G. 143 296
TOLSTIKOV G.A. 41 226 227 303	VALLE M. 414
TOLXDORFF C. 109	VAN BEEK J.A.M. 285
TOMÁS M. 283	VAN DER GRAAF T. 161
TOM DIECK H. 115 306 371	VAN DER SLUYS L.S. 114
TOMERIUS I. 25	VAN DIJK H.K. 324
TÓRÓS S. 359	VAN KOTEN G. 33 45 215 275 285 364
TORRENS MIGUEL H. 337	384
TOTTIE L. 374	VAN LEIJEN M. 389
TOUPET L. 43 205 408 441	VARGAS M.D. 16
TRALDI P. 280	VARSHNEY A.K. 237
TRAVERSO O. 281	VASAPOLLO G. 279
TREMONT S.J. 298	VÁZQUEZ DE MIGUEL A. 58
TROVARELLI A. 362	VČELÁK J. 110
TSCHINKE V. 17 348	VEGAS A. 154
TSUJI J. 1	VENZO A. 122 271 342
TUBA Z. 359	VERGAMINI P. 114
TUMANSKAYA A. 341	VERLHAC J.-B. 307
TURPEINEN U. 169	VERPEAUX J.-N. 170
	VERSCHUUREN A.H.M. 364
	VERSLUIS L. 347
UBEDA M.A. 434	VESSEY J. 332
UCHIDA T. 187	VESZPRÉMI T. 88
UCHIDA Y. 187	VETTORI U. 224
UGLIENGO P. 345	VICENTE J. 236 290 292 293
UGOZZOLI F. 431	VICHI E.J.S. 310 343
ULLENIUS C. 119 287	VIHANTO J. 244
UNGVÁRY F. 60	VILLAFANE F. 53
USIATINSKY A.YA. 229	VILLENEUVE P. 176
USÓN R. 283	VINAIXA J. 273
USTYNYUK N.A. 422	VIOLANO L. 388
	VITAGLIANO A. 4 309

VITALI F. 30  
VITERBO D. 345  
VITULLI G. 106  
VIZZA F. 198 432  
VOICULESCU N. 228  
VOLPE A. 39  
VOLPE P. 414  
VOL'PIN M. 107 147  
VON PHILIPSBORN W. 325 418  
VOSTRIKOVA O.S. 303  
VRIEZE K. 45 270 285 384 389  
VYSHINSKAYA L.I. 420

WU F.-J. 48  
WU R.F. 11  
  
YABLOKOV V.A. 351  
YANG X. 3  
YANOVSKY A. 147  
YAOUANC J.J. 357  
YE C. 138  
YEH S.-K. 54 329  
YOUNGDHAL K.A. 344

WACHTLER U. 231  
WADEPOHL H. 159  
WAGNER I. 136  
WANG D.L. 29  
WANG J. 202  
WANG Q. 87  
WANG Y. 54  
WARDELL J.L. 177  
WARHURST N.J.W. 61  
WÄRNMARK K. 417  
WASSINK B. 447  
WEISS E. 90  
WERNER H. 336 439  
WHALLEY J.M. 340  
WHITTLESEY M. 332  
WHITTON A.J. 74  
WIELSTRA Y. 265  
WILKINSON D. 126  
WILKINSON G. 112  
WILLEM R. 86  
WILLIAMS I.D. 157  
WILLIS A.C. 282  
WOOLHOUSE C. 311  
WRIGHT A.H. 149 333 425  
WRIGHT L.J. 78

ZAKHAROV L.N. 140  
ZAKI A. 184  
ZAKI A.B. 356  
ZANATHY L. 248  
ZANAZZI P.F. 369  
ZANELLA P. 413  
ZANELLO P. 47 175  
ZANI P. 398  
ZANOBINI F. 432  
ZANONATO P.L. 143  
ZANOTTI V. 167  
ZANOTTO L. 277  
ZARGARIAN D. 157  
ZELLNER K. 243  
ZELYAEV I.A. 351  
ZENNECK U. 109  
ZHANG Z. 195  
ZHAO S.-K. 211  
ZHAO Y.-Z. 233  
ZHIL'TSOV S.F. 294 295 412  
ZIEGLER M.L. 322  
ZIEGLER T. 17 347 348  
ZWETTLER R. 440